Volume 54 September–October 1959 Number 6

Economic Geology

and the

Bulletin of the Society of Economic Geologists

CONTENTS

Mineral Assemblages in Sulfide Ores: The System Cu-Fe-S-O ..... *Hugh McKinstry* 975
Ore Genesis in the Naica District, Chihuahua, Mexico ..... *John G. Stone* 1002
The Solubility of Zinc Sulfide in Water At High Temperatures ..... *A. J. Ellis* 1035
Effect of FeS on the Unit Cell Edge of Sphalerite. A Revision ..... *B. J. Skinner, P. B. Barton, Jr., and G. Kullerud* 1040
Quantitative Mineralogy in 30 Minutes ..... *J. P. Lyon, W. M. Tuddenham, and C. S. Thompson* 1047
Spontaneous Polarization Potentials and Clay and Limonite Deposits in the Gatesburg Formation of Central Pennsylvania ..... *Gerardo W. Gross and E. James Moore* 1056
Physical and Chemical Properties of the Petrographic Components of a High Volatile Bituminous Coal ..... *S. Ergun, J. T. McCartney and M. Mentser* 1068
Manganese Deposits of Hungary ..... *Magdalene Drubina-Szabo* 1078
The Alteration of Ilmenite ..... *M. D. Karkhanavala and A. C. Momin* 1095
A Beryllium Detector for Field Exploration ..... *George M. Brownell* 1103
Note on Some Cassiterite-Bearing Pegmatites Near Brandberg, South West Africa ..... *John G. Dennis* 1115

Scientific Communications:
The Application of Eh-pH Data to Metasomatic Deposits ..... *Jerome F. Machamer* 1122

Discussions:
Copper Uranium Deposits in Pennsylvania ..... *Edwin H. Gaucher* 1126
The White Pine Copper Deposit ..... *Ira B. Joralemon* 1127
Ore Deposits at Santa Barbara, Mexico ..... *George C. Selfridge* 1127

Reviews:
Translations of Recent Russian Literature ..... *C. F. Davidson* 1129
Geologia Applicata alla Ingegneria (A. Desio) 1130
Vector Space and Its Application in Crystal-Structure Investigation (M. I. Buerger) 1130
The Canadian Northwest: Its Potentialities (F. H. Underhill, Ed.) 1130
Environmental Conservation (R. F. Dasmann) 1131
Mineralogy, An Introduction to the Study of Minerals and Crystals (E. H. Kraus, W. F. Hunt and L. S. Ramsdell) 1131
Books Received ..... *John W. Cotton and Cyrus W. Field* 1131

Society of Economic Geologists 1139
Scientific Notes and News 1148

PUBLISHED SEMI-QUARTERLY

Six Dollars Fifty Cents a Year, One Dollar Twenty-five Cents a Copy

THE ECONOMIC GEOLOGY PUBLISHING COMPANY

Printed by Lancaster Press, Inc., Prince and Lemon Streets, Lancaster, Pa.

Second-class postage paid at Lancaster, Pa.

Economic Geology

and the

Bulletin of the Society of Economic Geologists

Issued Semi-Quarterly (Jan.–Feb., Mar.–Apr., May, June–July, Aug., Sept.–Oct., Nov. and Dec.) and sent to subscribers on or about the following dates: February 1, March 15, May 1, June 15, August 1, September 15, November 1, December 15.

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Foreign Agents. The Technical Bookshop, Salisbury House, London Wall, London E. C. 2, England, British Agents.

Indexed in the Industrial Arts Index.

LANCASTER PRESS, INC., LANCASTER, PA.

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AND THE

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ECONOMIC GEOLOGY

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BULLETIN OF THE SOCIETY OF
ECONOMIC GEOLOGISTS

VOL. 54 SEPTEMBER–OCTOBER, 1959 NO. 6

MINERAL ASSEMBLAGES IN SULFIDE ORES: THE SYSTEM Cu-Fe-S-O

HUGH McKINSTRY

CONTENTS

	PAGE
Introduction	976
Binary system Cu-Fe	978
Binary system Cu-S	978
Binary system Fe-S	980
Ternary system Cu-Fe-S	981
Ternary system Fe-S-O	989
Ternary system Cu-S-O	990
Ternary system Cu-Fe-O	991
Quaternary system Cu-Fe-S-O	992
Discussion	994
Acknowledgments	997
Appendix	998
References	998

ABSTRACT

The paper presents the evidence supporting ternary phase diagrams proposed in earlier articles and builds a quaternary diagram making use of observed mineral associations to supplement available chemical data.

Phase relations explain the rarity or absence of a number of associations such as magnetite-covellite, pyrrhotite-hematite and, in the presence of magnetite, bornite-pyrite.

Although most commonly observed assemblages are apparently stable over a wide range of temperature there is a strong suggestion of shifting of tie-lines with change of temperature within the field of composition bounded by chalcocite, covellite, chalcopyrite, and pyrite.

The observed sequence in ore deposition is not so much a sequence of individual minerals as a sequence of assemblages, each higher than the preceding one in ratio of sulfur to oxygen and usually of copper to iron. However, it seldom reaches the ultimate high-sulfur assemblage, covellite-pyrite. Late stage reversals of the trend (e.g., chalcocite replacing covel-

lite) could be occasioned by waning of sulfur supply before cooling was far advanced. Certain minerals such as pyrrhotite and magnetite are early members of the sequence not because they are in themselves "high temperature" minerals but because they are stable in low-sulfur high-iron assemblages.

INTRODUCTION

THE common sulfide minerals of copper ores are phases belonging to the system Cu-Fe-S. As they are accompanied at many localities by magnetite or hematite and as their oxidation products include oxides of iron and copper it is pertinent to observe also the phase relations in the quaternary system Cu-Fe-S-O.[1]

Apart from this system the only primary ore minerals of copper belong to the system Cu-Fe-As-S.[2] It is true that sulfides of other metals are commonly present in copper ores but the most ubiquitous of these, lead, zinc, and molybdenum, do not combine with iron or copper to form ternary or quaternary phases except for the varying amounts of iron and copper in some sphalerites.

Although the system Cu-Fe-S-O includes about a dozen mineral phases the number of them that could occur stably together is limited by Gibbs' phase rule to six and at random temperature and pressure the maximum number of phases would ordinarily be four, one of which, in a simple system at low pressure, would be a vapor phase. In the more complex natural systems one or more fluid phases would be present during deposition so that ordinarily not more than three mineral phases from this system would be expected to occur in equilibrium with each other.

If the phase relations within the system were completely known it would be possible to predict which minerals could occur together under given conditions. Conversely the assemblage of coexisting minerals would tell a great deal about the physical and chemical conditions under which an ore was deposited. Work in progress at the Geophysical Laboratory and elsewhere is providing much-needed data of this nature but the full investigation of a quaternary system is not a matter to be completed in a day or a year.

In any case if the results are to be applied to a natural system it is imperative to see what minerals actually occur together and in what types of ore deposits. In fact the large accumulation of observational data already available makes it possible to postulate tentative phase diagrams that are capable of explaining many facts of occurrence and of pointing to parts of the system that are most in need of elucidation. Naturally these diagrams are incomplete and subject to modifications as new information from the laboratories becomes available.

The quaternary model presented in this paper is built up from the four constituent ternary diagrams (Fig. 1). The binary systems Cu-Fe, Cu-S,

[1] A companion paper discussing the environment of formation of minerals in this quaternary system will be presented by R. M. Garrels and R. Natarajan.

[2] Copper-antimony sulfides, notably tetrahedrite, although important ores of silver, are mined in few if any places primarily for their copper content.

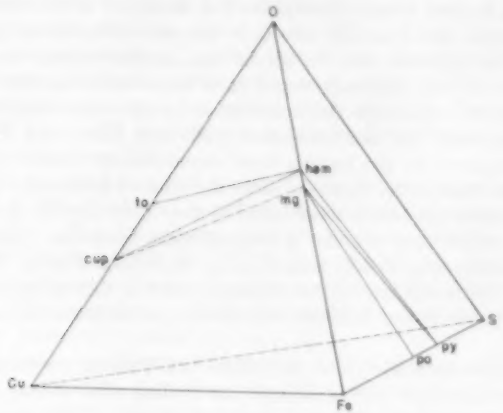

FIG. 1. Model for the system Cu-Fe-S-O. (Joins are shown only on visible faces.)

and Fe-S are used to construct the ternary diagram Cu-Fe-S and to this the ternary diagrams Cu-S-O, Fe-S-O, and Cu-Fe-O are added. Although all of these have the form of isothermal phase diagrams, they are not labelled here with any specific temperature. Each is valid for a range of temperature insofar as no change of tie-lines takes place within that range. A few changes of this sort are possible and will be discussed.

Limitations.—Lack of tie-lines in certain places where geometry or chemical relations would require them is an intentional admission of ignorance. Furthermore no attempt is made to show the complete relations of solid solutions, important as they are, since their limits, especially at the temperatures of greatest geological interest have been very incompletely defined. In this connection a consideration sometimes overlooked is that in general the temperature of unmixing of a solid solution is not a fixed point but varies with the composition of the original mix crystal, which, in turn may be an indication of its own temperature of crystallization.

Criteria.—A few of the tie-lines shown are established by experimental evidence. The rest have been drawn to connect minerals that commonly occur together and to separate those that habitually do not. It is true that co-occurrence is not a guarantee of compatibility, even where there is evidence that the two minerals in question were deposited simultaneously (and such evidence is rare); while there are accepted criteria, varying in reliability, for determining order of deposition or crystallization, the criteria of contemporaneous deposition are few and uncertain. However, two minerals in contact with each other without any indication of an intermediate phase seems a good indication of compatibility.

The fact that one mineral has partly replaced another is an indication that conditions were changing during or after deposition, consequently the sequence

can give an indication of the direction of the change. Where evidence favors a gradual change—not a drastic one as in the case of oxidation or enrichment superimposed on primary ore—it seems tenable that where one mineral replaces another the two minerals would have been stable together if conditions had *not* changed. Although this criterion is by no means infallible it usually leads to conclusions that are consistent with each other and in accord with such phase relations as are known from experimental work.

Conventions and Abbreviations.—For the sake of uniformity in designating systems, elemental components are listed in the order Cu, Fe, S, O, this being the order in which they appear in conventional formulae. Compounds are listed in corresponding order, thus Cu_xS_y, $Cu_xFe_yS_z$, Fe_xS_y, Cu_xO_y, Fe_xO_y. Within these limitations, phases are listed in order of increasing sulfur-content. However this rule is not followed rigidly at the expense of convenience in presentation.

Abbreviations used in figures and tables are those recommended by Chace (22) with the exception that cp is used for chalcopyrite, a usage which Chace has agreed to sanction (personal communication). His list, based on a number of abbreviations already in wide use and carefully worked out to avoid duplications, might well be adopted as a universal standard in labeling diagrams and photomicrographs. Except in the case of chemical symbols of the elements these abbreviations begin with *lower case* letters. This avoids confusion between, say, Mg for magnesium and mg for magnetite. An alphabetical list of abbreviations used in this paper is given in the Appendix.

Solid solutions are designated by placing the end-members in parentheses separated by a comma, thus (cp,cn) represents a solid solution phase intermediate in composition between chalcopyrite and cubanite.

BINARY SYSTEM Cu-Fe

Apart from the native elements no mineral phases exist in this binary system. Mutual solid solution between metallic copper and metallic iron is extremely limited below 800° C (Daniloff, 1948).

BINARY SYSTEM Cu-S

Minerals	Formula	Abbreviation
Cu (native)	Cu	Cu
Chalcocite	Cu_2S	cc
Digenite	Cu_9S_5	di
Covellite	CuS	cv

Chalcocite exists in two modifications with a transition point at 90° ± 5 according to Buerger or at about 105° according to Kullerud (48). Low chalcocite is orthorhombic and high chalcocite is hexagonal.

Digenite is rhombohedral at low temperatures but inverts to a cubic form at 58° C (49). "Octahedrons" of synthetic digenite prepared above this temperature but studied at room temperature consist of eight rhombohedral crystals (25).

Digenite has been synthesized at temperatures as low as 25° C and is stable in the presence of excess sulfur up to 925°. At this temperature, and a pressure as yet undetermined but less than 65 at., there is a quadruple point at which digenite, chalcocite, liquid sulfur and sulfur vapor can coexist. At higher temperatures, pressure has only a small effect on dissociation so that even at 30,000 psi (2,000 at.) digenite would probably break down at a temperature no greater than 350° C (47).

Covellite is essentially stoichiometric CuS. When heated to a temperature somewhere below 235° C, covellite begins breaking down into digenite and sulfur vapor. The dissociation pressure increases sharply with temperature up to an invariant point at 507° ± 3° and 880 mm Hg total pressure (1.16 at.) where the four phases, digenite, covellite, sulfur (liquid), and sulfur (vapor) are stable together. Above this point the dissociation temperature increases very little with further pressure (57).

Solid Solutions.—Kullerud (47) reports that chalcocite can take up sulfur (or digenite) in amounts that increase with temperature up to 925° C, but decline at still higher temperature and do not give the complete solid-solution series indicated by Merwin and Lombard (61). At 925° the sulfur content may reach 21 percent by weight, corresponding to $Cu_2S_{1.05}$. At 600 degrees the maximum sulfur content of chalcocite is 20.5 percent, i.e., about $Cu_2S_{1.02}$.

At the other end of this range, Kullerud finds no measurable solubility of chalcocite (or copper) in digenite.

On the side toward the composition of covellite, digenite can take up sulfur but the maximum amount (at 450° C) is only 0.4 percent by weight in excess of the ideal composition Cu_9S_5, thus extending to $Cu_9S_{5.122}$. The amount decreases with lowered temperature but Kullerud's diagram does not show the break at 78° nor the stoichiometric composition below this reported earlier by N. Buerger (15).

In short, the simple copper sulfides show only limited fields of solid solution among themselves in contrast to the ready solubility of chalcocite and digenite in bornite at moderate temperatures.

Collinearities.—Because of their compositions the following pairs would not be expected together: Native copper and digenite, chalcocite and covellite, digenite and native sulfur. Contrary to expectation, chalcocite and covellite do occur together and not uncommonly. At Butte, hypogene covellite occurs chiefly if not exclusively in digenite-bearing ore but in some instances chalcocite is present as well. "Covellite occurs in the chalcocite as minute plates arranged in a crudely triangular pattern" (71, p. 474). While it may be maintained that the two are not contemporaneous, the fact remains that they have not interacted to form digenite.

In secondarily enriched ores from many localities, all definitely supergene chalcocite x-rayed by Wandke (97) whether associated with digenite or not, proved to be true chalcocite. Even some blue chalcocite that looked like digenite proved on x-ray analysis to be chalcocite. Lacking any better explanation it must be concluded that the association is metastable.

BINARY SYSTEM Fe-S

Minerals	Formula	Abbreviation
Native iron	Fe	Fe
Pyrrhotite	$Fe_{1-x}S$	po
Pyrite	FeS_2	py
Marcasite	FeS_2	ms
Smythite	Fe_3S_4	
Sulfur	S	S

The name *pyrrhotite* applies to ferrous sulfides ranging in composition from FeS to about Fe_7S_8. Altogether at least three low-temperature and three higher temperature modifications have been indicated but there is lack of unanimity among authorities in regard to nomenclature if not in regard to identity of the phases themselves. Among the low temperature phases, one of composition close to FeS (β_1 of Gronvold and Haraldsen, 37) is hexagonal and paramagnetic. The phase at the low-iron end of the composition range is ferromagnetic and monoclinic or orthorhombic (18). The change in crystal structure appears when the iron content falls below 49 percent (atomic) but ferromagnetism does not appear until Fe declines to 48 percent.

On heating, the β_1 (FeS) phase inverts at 138° but with lower iron content this inversion point is apparently lowered. Other inversions have been reported at 360° (37) and 650° (38). However, Arnold (2a) finds no discontinuity in the composition curve of sulfur-saturated pyrrhotite anywhere between 325° and the invariant point at 743° C. On quenching from above 666° sulfur-rich pyrrhotite exsolved lamellae whose identity has not been determined. The resulting textures resemble those described in natural pyrrhotites by Scholtz (74) and others.

Pyrite and *marcasite* are generally considered dimorphous although Buerger (16) proposed that marcasite was slightly deficient in sulfur. At low temperatures marcasite must be metastable as it has a higher free energy of formation [3] than pyrite. It is formed, in some instances at least, by rapid precipitation after which it presumably inverts slowly to pyrite. Pseudomorphs of pyrite after marcasite are common but the reverse is rare.

Smythite is very rare or at least has rarely been recognized, and has been found only in deposits formed at very low temperature. It occurs in geodes along with the monoclinic ferromagnetic variety of pyrrhotite and earlier pyrite in Indiana where its temperature of deposition is estimated as between 25 and 40° C (28). In an occurrence at Kramer, Cal., Christ and Garrels (31) calculated that the environment was never hotter than 70° C.

Pyrite-Pyrrhotite Relationships.—Pyrite dissociates into pyrrhotite and sulfur at atmospheric pressure and a temperature of 689° C. (At lower pressure of S-vapor the temperature of equilibrium is still lower—575° at about .001 [0.75 mm ± 0.25 Hg]) (1). The dissociation temperature increases with pressure up to 743° ± 3° and about 12.2 at. (180 psi), an invariant point at which pyrite, pyrrhotite and sulfur vapor are in equilibrium

[3] Free energy of formation of marcasite at 298° K as computed by R. Natarajan from data given by Latimer (53) is − 34 kilocalories. Free energy for pyrite as given by Kelley (45, p. 406) is − 36.07.

with a liquid, largely sulfur. Above this point, higher pressure increases the dissociation temperature only moderately since no vapor is present, raising it to only 815° C at 5,100 at. (75,000 psi) (50). Arnold (2) states that pyrrhotites coexisting with pyrite show increasing iron omission with increasing temperature, Fe falling to about 46 atomic percent at 600° C.

Observed Associations.—Pyrite and *pyrrhotite* are common associates. Pyrite is often reported as the earlier of the two (82) but some inferences as to sequence are based on euhedral form of the pyrite, an unreliable criterion susceptible to exactly the opposite interpretation (39). It is true that there are many instances of pyrite crystals veined or rounded by the enclosing pyrrhotite, but there are also numerous textures indicative of pyrite later than pyrrhotite.

Pyrrhotite and *smythite* (see above).

TERNARY SYSTEM Cu-Fe-S

Phase diagrams for portions of the ternary system at high temperatures have been prepared from experimental data by Merwin and Lombard (61), Schlegel and Schuler (73), and by Grieg, Jensen, and Merwin (36). For lower temperatures, more applicable to most ore deposits, inferred phase diagrams have been published by Betekhtin, (11), McKinstry and Kennedy (60) and Bartholomé (4, 5). These, although prepared quite independently of each other, agree reasonably well in general features but differ in certain aspects that will be discussed.

Minerals.—Three-component minerals in the ternary system Cu-Fe-S are:

	Formula	Abbreviation
Bornite	Cu_5FeS_4	bn
Chalcopyrite	$CuFeS_2$	cp
Cubanite	$CuFe_2S_3$	cn
Valleriite	$Cu_2Fe_3S_7$ (?)	

Bornite, as indicated by Kullerud and Roseboom (49) is orthorhombic at low temperature but inverts to a cubic form at about 190° C. (Fruh [29] had reported earlier that the transition to the disordered form began at 170° and was complete at 220°.)

Chalcopyrite, tetragonal, becomes disordered at a high temperature which Cheriton (23) by using a heating camera has determined as 580° ± 20°. This corresponds roughly to an exothermic peak which he observed at 530° by means of differential thermal analysis. Hiller and Probsthain place the transition at 550° (41).

Cubanite, orthorhombic, occurs characteristically in deposits of presumed high-temperature origin where it is generally intergrown with chalcopyrite or less commonly with pyrrhotite.

Valleriite is a mineral of uncertain composition. It is presumed to consist of Cu, Fe, and S but the proportions 2:4:7, 3:4:7, and 2:3:7 have all been proposed. On account of its sparse occurrence and for other reasons, Bartholomé (5, p. 22) questions whether it is even a part of the simple Cu-Fe-S system.

Chalcopyrrhotite is not recognized in Dana (66) as a distinct mineral species. A compound, unstable below 225° C according to Borchert (12), has been assigned compositions of $CuFe_4S_5$ and $CuFe_4S_6$ but Ramdohr (68) considers it a solid solution that may range from the composition of cubanite ($CuFe_2S_3$) to $CuFe_7S_8$.

Until definite compositions or ranges of composition are established for valleriite and chalcopyrrhotite any attempt to show them on phase diagrams would merely compound the present uncertainties.

Solid Solutions.—Most of the controlled investigations of fields of solid solutions involving ternary phases have been at temperatures not far below those at which they melt or dissociate. At lower temperatures, more pertinent to natural assemblages, the fields of solid solution have been partially explored, chiefly by heating natural mixtures and intergrowths. While the fields have not been delimited either as to temperature or composition, mutual solubilities of certain minerals have been established.

Chalcocite-Bornite.—Bornite dissolves in chalcocite, at least in limited amounts, at temperatures as low as 100° C (70). Apparently solubility increases up to 350°, the highest temperature of Schwartz' (78, 79) investigations, and has become complete ("chalcocite solid solution") at some temperature below the melting point (900° +) (61).

Schwartz was able to homogenize, at 225°, mixtures containing 5 to 15 percent of bornite but when, on the other hand, the proportion of chalcocite was small, the chalcocite turned much darker but did not disappear, while the larger enclosing area of bornite was not noticeably changed in appearance. It may be inferred that the chalcocite took up bornite until it was saturated but the amount was insufficient to modify the large area of bornite appreciably.

On cooling, the artificial solid solutions unmixed to grating textures consisting of chalcocite blades enclosing triangular areas of bornite or of bornite-chalcocite [4] intergrowth. It would appear then that the field of solid solution is more extended at the chalcocite than at the bornite end of the series and that the solid solution fields converge with increasing temperature. Solubilities at the bornite end and, in fact, all quantitative variations with temperature, remain to be determined.

Digenite-Bornite.—Kullerud and Roseboom (49) find that in the presence of a sulfur-rich liquid digenite can take iron into solid solution which reaches the composition of bornite at 540° C. If, however, the composition of the charge lies on the digenite-bornite join, complete solid solution exists down to about 400° C.

Bornite-Chalcopyrite.—Schwartz produced mutual solid solution of chalcocite and bornite at 475° but not at 450° (80). With lowering of temperature unmixing was rapid; when cooled through a period of 24 hours chalcopyrite separated out as discrete grains or as discontinuous rims around grains of bornite. Only by very quick cooling could grid textures be retained. Ex-

[4] As the experiments antedated the rediscovery of digenite, this mineral was not designated as such but in some experiments, notably where the proportion of bornite was less than 3%, two kinds of "chalcocite," blue and white were intergrown.

cellent photographs of artificial exsolution textures are presented by Latsky (54).

Chalcopyrite-Pyrrhotite.—Chalcopyrite and pyrrhotite do not form a continuous series at high temperatures, i.e., those in the neighborhood of their eutectic point (about 920°) (61 and 73). Instead there is a gap between (a) pyrrhotite which takes up only a very small amount of copper, not more than 1.5 atomic percent under conditions of Merwin and Lombard's experiments and (b) "chalcopyrite solid solution" which can take up FeS to about the composition of cubanite ($CuFe_2S_3$) (61). Roseboom and Kullerud (70a) report that at 700° C in the presence of sulfur-rich liquid this solid solution can form a continuous phase from the ratio Cu_6Fe_4 to Cu_3Fe_7, but it does not extend to pyrrhotite. This calls for reappraisal of the continuous phase from chalcopyrite to pyrrhotite inferred by Borchert (12). That chalcopyrite-cubanite intergrowths could be homogenized on heating and unmix on cooling had been shown earlier by Schwartz (77) and by Hewitt (40).

Although Borchert (12) postulated breakdown of "chalcopyrrhotite solid solution" in a succession of exsolution phenomena at successive declining temperatures, yielding two or more of the minerals: chalcopyrite, cubanite, valleriite, pyrrhotite, detailed relationships in this part of the system are still not clear and await the results of experiments under controlled conditions of sulfur vapor pressure. Thus if cubanite remains stable below 225° C, as indicated by Borchert, how can it be absent in a chalcopyrite-pyrrhotite ore as at Noranda? And how, for that matter, can both chalcopyrite and pyrrhotite occur *with* cubanite as at most cubanite localities?

Mineral associations suggest that the answer may lie in sulfur content. If cubanite is a stoichiometric compound, its composition, which may be written $CuFeS_2 \cdot FeS$, lies on a line between chalcopyrite and FeS and is not collinear with chalcopyrite and high-sulfur pyrrhotite. Thus a high-temperature field, pyrite-pyrrhotite-solid solution (cp,cn) (Fig. 3a) would give place at lower temperature to two fields: (a) chalcopyrite-cubanite-pyrrhotite and (b) chalcopyrite-pyrrhotite-pyrite (Fig. 3b). This would explain not only the coexistence of chalcopyrite and pyrrhotite together with cubanite if the sulfur content of the assemblage is low and without it if the sulfur content is higher, but also such occurrences as that described by Schwartz (76) at Fierro, New Mexico where a lath of cubanite contains corroded remnants of pyrite. Bartholomé (5) appears to have reached a somewhat similar conclusion.

Collinearities.—Plotting of mineral compositions in the ternary system Cu-Fe-S (Fig. 2) reveals collinear relations that would preclude certain associations:

Collinearity	Precludes
cc, bn, cp	cc, -cp
Cu, cp, py	Cu-py
cv, cp, cn, FeS	cv-cn
	cp-FeS

These collinearities readily explain some recognized incompatibilities. Bateman (7, p. 141) remarked long ago that at Bristol, Conn., "Generally chalco-

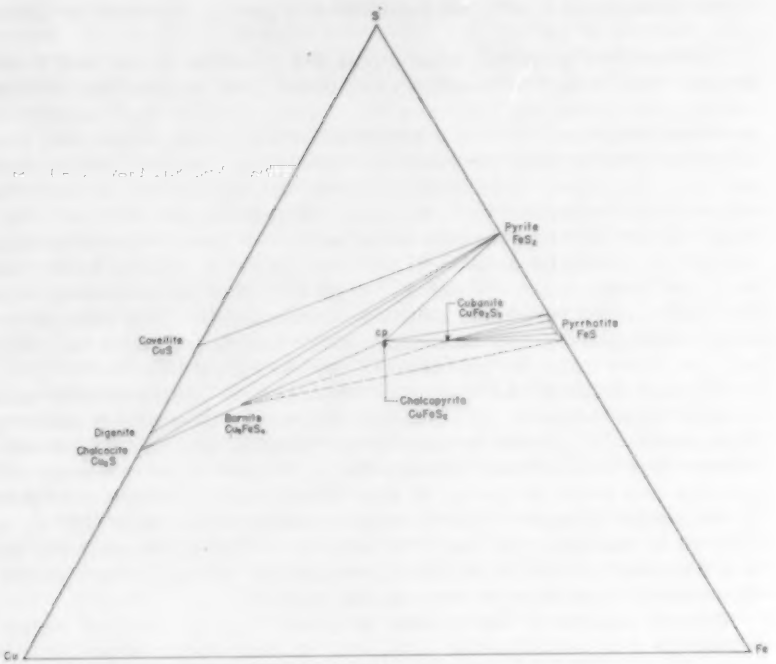

FIG. 2. System Cu-Fe-S. (Proposed phase diagram.)

pyrite and chalcocite do not occur in the same specimen in appreciable amounts." Pyrite is notably absent in native copper deposits and the association covellite-cubanite is unknown.[5] While a collinearity would prevent co-occurrence of chalcopyrite and pure FeS it would not preclude the association chalcopyrite-pyrrhotite.

Observed Associations.—Chalcocite-bornite and *Bornite-chalcopyrite* are very common assemblages.

Bornite-pyrite is also common. Although in some instances chalcopyrite forms as an intermediate product as described at Butte by Ray (70, p. 463 ff.), there are other instances of direct association in this district (e.g., 6, Fig. 18, p. 592 as well as at Magma (86, p. 200) Bisbee, and Patagonia, Arizona (35, p. 215). In some cases, pyrite is replaced by what are now mixtures of bornite and chalcocite as at Mt. Lyell, Tasmania (26, Fig. 132) and Magma (86, Plate XXD).

These occurrences are cited here because the validity of a bornite-pyrite tie-line has been questioned. Bartholomé prefers the precluding ties covellite-

[5] All positive statements of this sort should be understood to carry the qualification "so far as the writer is aware" which, however, will be omitted to avoid undue monotony.

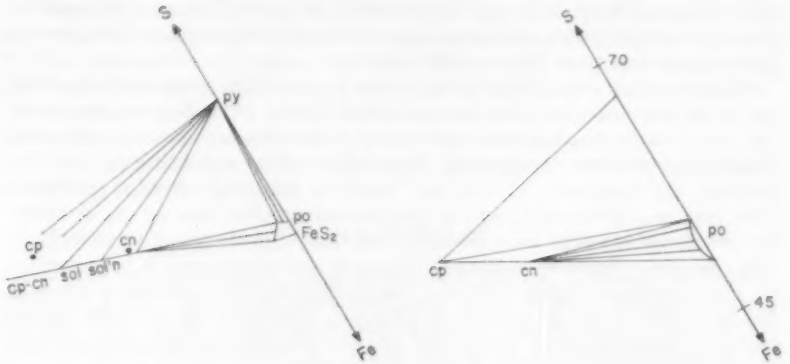

FIG. 3. Portion of the system Cu-Fe-S. Left: At high temperature. Right: At lower (mesothermal) temperatures.

chalcopyrite and pyrite-digenite (to be discussed later) and suggests that the apparent compatibility of bornite and pyrite is to be explained by sluggishness of pyrite in reacting with other sulfides. However, in "exploded bomb" and other replacement textures pyrite has definitely been attacked and corroded, with no sign of covellite or digenite as intermediate products, hence it must not have been inert at the time the textures were formed.

The impression that bornite and pyrite are antipathetic may arise from the fact that they would not be stable together in the presence of magnetite, as noted in the discussion of the quaternary system Cu-Fe-S-O.

Chalcocite-Pyrite.—Although not very common elsewhere, this association is present in much of the Central Zone at Butte, where the chalcocite occurs largely in a chalcocite-bornite intergrowth, suggesting that pyrite was replaced by "chalcocite solid solution." Only in certain types of ore does digenite accompany the chalcocite.

Digenite-Pyrite.—The mineral associations of digenite are not well known from natural assemblages as the mineral was not recognized as such before N. W. Buerger's study published in 1941 (15). Even after that not all descriptions employed x-ray methods to distinguish between digenite and chalcocite. Digenite associations have been best studied at Butte where pyrite is closely associated with it in some of the deep-level ore; much of the digenite is intergrown with chalcocite and minor amounts of bornite.

Covellite-Pyrite.—This association although not very common is definitely observed at Butte. It is not only required by geometry of the diagram but was established at 411° (at 455 mm S-pressure) and below by Merwin and Lombard's experiments (61).

Chalcopyrite-cubanite and *cubanite-pyrrhotite* are common associations but usually in intergrowths presumably originating from exsolution.

Alternative Associations.—Digenite-bornite intergrowths occur at Butte

(71) Magma (86, p. 102) and Kennecott[6] (10). At Butte and Magma the bornite and digenite are associated with chalcocite in three-phase intergrowths that suggest derivation from a solid solution.

Covellite-chalcopyrite intergrowths are rare in hypogene mineralization; one of the few examples is at Cananea where Kelley (46) observes that covellite, presumably hypogene, occurs along with chalcopyrite and chalcocite (digenite?) as rims along grain boundaries; other aggregates of the two minerals are lenticular. These are evidently late-stage reaction products. Chalcopyrite is generally absent in the primary covellite-bearing ore at Butte. In secondarily enriched ores, direct replacement of chalcopyrite by covellite is very common. Stability of this assemblage at low temperature is suggested by the experiments of Sugaki (90) who heated chalcopyrite-covellite intergrowths and up to 200° C got no reaction in 12 hours. Between 300 and 350 degrees grains of pyrite appeared and at 375 degrees covellite had disappeared completely with development of a bornite-like mineral.

Covellite-bornite intergrowths are also rare in hypogene ores. At Kennecott (9) covellite laths occur with chalcopyrite and bornite and at Tsumeb (63) covellite occurs along with bornite and "chalcocite." In both cases the respective authors ascribe the textures to unmixing of solid solution.

But replacement of bornite by covellite under supergene conditions is very common. Among many examples is the clear description at Butte by Locke, Hall, and Short (58, p. 20) of covellite replacing bornite in rosettes and along cracks and vein boundaries. Other examples are found at Bristol, Conn. (7), where covellite occurs along with chalcopyrite in cracks in bornite, and Magma, Ariz., where covellite occurs as veinlets or rosettes generally as a replacement of bornite (86). In fact bornite is, if anything, more susceptible to covellite replacement than is chalcopyrite. Graton and Murdoch (35, p. 767) in their study of textures of copper ores state that covellite "develops most commonly in bornite . . ." but "It readily forms also from chalcopyrite." Edwards (26, Fig. 120) shows an example from Fiji in which covellite selectively replaces bornite in preference to chalcopyrite. A similar example from Butte (58, p. 11, Fig. 2) shows covellite veinlets crossing bornite but halting at chalcopyrite. In this connection, Ramdohr (69, p. 524) remarks: "Interessant sind Entmischungsverwachsenen von Kupferkies und Bornit, wo die Covellinbildung viel schneller und selektiv den Bornit erfaszt." In short the evidence for a tie line covellite-bornite at low temperature seems fully as good as for covellite-chalcopyrite. This evidence is emphasized because of Bartholomé's contrary conclusion that covellite rarely replaces bornite directly (5, p. 16).

Discussion: Alternative Assemblages in the Field Digenite-Covellite-Bornite-Chalcopyrite.—To the assemblages chalcocite-pyrite and digenite-pyrite, three alternatives have been listed. One of these, digenite-bornite is not compatible with chalcocite-pyrite. The other two, covellite-bornite and covellite-chalcopyrite are not compatible with any of the foregoing.

[6] Identity of "crystalline chalcocite" at Kennecott and "blue isometric chalcocite" with digenite at Magma has been confirmed by A. Wandke, Jr. (97) by x-ray methods but at Magma, "blue chalcocite" also occurs which is not digenite.

These apparently anomalous assemblages may of course be metastable, an explanation not improbable under conditions of secondary enrichment and, in fact, inescapable in certain other associations such as chalcocite-covellite, chalcocite-chalcopyrite (granting bornite to be stable) and pyrite-marcasite. On the other hand each of the alternative assemblages may well be stable under its appropriate conditions of temperature and pressure.

The digenite-chalcopyrite association is alternative to chalcocite-pyrite in accordance with the equation:

$$5\ \text{cc} + \text{py} = \text{di} + \text{cp}.$$

Calculation of free energies, using the data for 298° K computed by Bartholomé (5, p. 25), favors the right hand side of the equation but by only 0.2 percent which is far within the stipulated limits of uncertainty. Comparison of volumes, however (at 25° C) shows that if the reaction proceeds to the right the volume increases by nearly 7 percent. Although data are not available for higher temperatures, the presumption is that with so little difference in free energy the reaction would be strongly influenced by pressure. I, therefore, suspect that at low pressures the tie-line digenite-chalcopyrite may be valid as indicated by Bartholomé (4 and 5) but that at high total pressure and not too high vapor pressure of sulfur the assemblage chalcocite-pyrite is stable as at Butte.

Similarly the reaction

$$7\ \text{cc} + \text{py} = \text{di} + \text{bn}$$

requires little change in free energy at constant pressure but a 5 percent increase in volume.

Examples in which pyrite is not involved are described by Vokes (95) in ores from northern Norway. His "copper paragenesis" is notable for absence of pyrite and, significantly, hematite with residual magnetite is present at least in some instances. The chief minerals are bornite and chalcopyrite, occurring in separate grains in some ores and as lamellar intergrowths in others. Bornite is replaced by digenite or in some cases digenite and covellite. In these replacements, bornite is attacked first, leaving chalcopyrite lamellae as residuals which may eventually succumb if they are sparse. In some specimens, lamellae of chalcopyrite in bornite are bordered by "light-colored bornite" and this in turn by a thin zone of digenite "worms," giving textures reminescent of the intergrowths in the Skaergaard intrusive (96, Fig. 8) where lamellae of chalcopyrite in a rectangular grid in bornite are bordered by rims of digenite. This suggests conversion of bornite to digenite-chalcopyrite by addition of sulfur and under other conditions to digenite and ultimately to covellite by removal of iron or addition of copper.

Considering evidence from many localities, it appears likely that within this field there is a shifting of tie-lines with declining temperature, very possibly influenced also by differences in total pressure. With fairly high temperature and heavy rock-pressure as at Butte the tie-line chalcocite-pyrite is

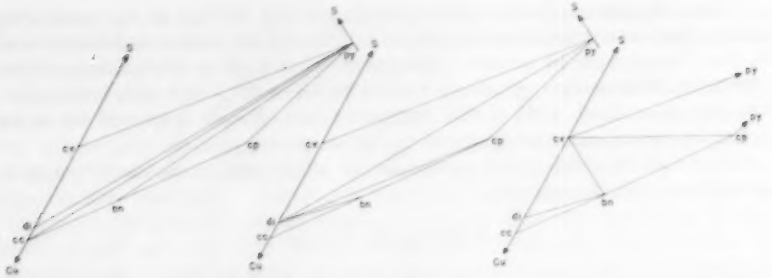

FIG. 4. Portion of the system Cu-Fe-S. Left: Under mesothermal conditions. Center: At lower temperature. Right: Under conditions of supergene oxidation.

valid (Fig. 4a). At lower temperature and perhaps lower total pressure this tie gives way to digenite-chalcopyrite (Fig. 4b). At still lower temperatures, notably but not exclusively those of supergene enrichment, digenite-chalcopyrite must be supplanted by covellite-bornite (Fig. 4c), otherwise covellite could not exist stably until all bornite had been converted to digenite-chalcopyrite or digenite-pyrite.

Doubtful Associations.—Ternary phase relations between native copper, native iron and the sulfides are not well known except at high temperatures. Schlegel and Schuler's diagram (73) for about 900° C shows tie-lines between bornite solid solution and both Cu and Fe. On the other hand, as mentioned by Bartholomé (1958) native copper and pyrrhotite have been observed together in meteorites. At variance with these and precluding all of them is a tie-line in Betekhtin's diagram (11, Fig. 27) between chalcocite and native iron, which may be justified by Schlegel and Schuler's equilibrium relations below about 650° C.

Natural assemblages do not provide evidence for or against validity of any of these joins. Native iron does not occur in ore deposits and native copper in the Lake Superior district is not found together with any of the copper iron sulfides (bornite and chalcopyrite are found in the district but not in association with native copper) nor is it associated in supergene products with sulfides other than chalcocite.

Bornite-Pyrrhotite.—The rarity of this association was long ago noted by Gilbert (32) and by Schwartz (82). It would be precluded by a join native copper-cubanite, an association reported in mattes (5, p. 14) but not expressed in natural assemblages, and by the rare association bornite-cubanite (65). It seems likely that under natural conditions, where water or CO_2 is present iron would react with them to form magnetite or hematite. Thus in the presence of available oxygen the assemblage chalcopyrite-magnetite is more stable and common:

$$18\ \text{po} + 3\ \text{bn} + 8\ \text{O} = 15\ \text{cp} + 2\ \text{mg}$$

Summary: Cu-Fe-S.—

Observed Assemblages:

Cu-cc	bn-cp
cc-di	bn-py
di-cv	cp-po
cc-bn	cp-cn
cc-py	cn-po
di-py	cp-py
cv-py	po-py

Three-Phase Fields:

cn-bn-py	bn-cp-py
cc-di-py	cp-cn-po
di-cv-py	cp-po-py

Alternative Three-Phase Fields:

cc-di-bn	di-cv-bn
di-bn-cp	cv-bn-cp
di-cp-py	cv-cp-py
di-bn-cp	

Assemblages Reported by other Authors:

Cu-bn	Bartholomé	in mattes
Cu-po	Bartholomé	in mattes
Cu-cn	Bartholomé	in mattes
Fe-cc	Betecktin	

TERNARY SYSTEM Fe-S-O (FIG. 5, UPPER RIGHT)

Minerals (other than those in the Cu-Fe-S System):

	Formula	*Abbreviation*
Magnetite	Fe_3O_4	mg
Hematite	Fe_2O_3	hem

Martite is a pseudomorph of Fe_2O_3 after magnetite. Maghemite, Fe_2O_3, crystallographically related to magnetite, is found typically as a product of oxidation rather than in hypogene ore deposits (66).

Kullerud's diagram (50) for this system below ca. 675° based on experimental determinations is identical, except for the fact that it includes SO_2, and, above 550°, FeO, with the diagram proposed by McKinstry and Kennedy (60) based on natural occurrences and is analogous to that of Betekhtin (his figure 23). Its main feature is that pyrrhotite and hematite do not occur together as noted earlier by Gilbert (33) whereas pyrite occurs with either magnetite or hematite and sometimes with both. Kullerud's diagrams at temperature above 675° showing a field pyrrhotite-pyrite-hematite, or (above ca. 700) pyrrhotite-magnetite-hematite are rarely, if ever, reflected in sulfide ores whether because the ores solidified at temperatures below 675° or because activities of sulfur and oxygen were not simultaneously high enough at these temperatures.

Summary: Fe-S-O.—

Observed Associations	*Three-Phase Fields*
po-mg	po-py-mg
py-mg	py-mg-hem
py-hem	

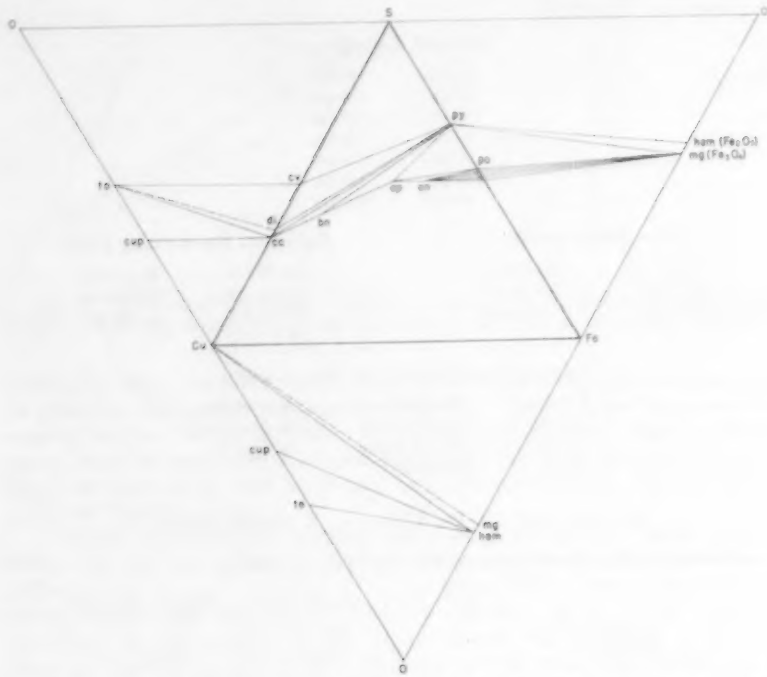

FIG. 5. Ternary systems in the quaternary system Cu-Fe-S-O. To form the tetrahedral model, fold up the outer triangles so that their apices meet at O.

TERNARY SYSTEM Cu-S-O (FIG. 5, UPPER LEFT)

Minerals.—Minerals of this system aside from native copper and the sulfides themselves are limited to oxidized zones.

	Formula	*Abbreviation*
Cuprite	Cu_2O	cup
Tenorite	CuO	to

Malaconite is an earthy form of tenorite. "Copper pitch ore" is apparently an impure copper oxide related to tenorite but containing manganese and other elements.

While cuprous and cupric sulfates if anhydrous belong in this system, the naturally-occurring sulfates of copper are hydrous and would appear only in the system Cu-S-O-H.

Observed Associations.—Cuprite occurs very commonly as a direct oxidation product of *native copper* or *chalcocite;* or cuprite and native copper may form together from oxidation of chalcocite as at Clifton-Morenci, Ariz. (55) and Chuquicamata (42, p. 254).

Chalcocite-tenorite is not a particularly common association but is observed at Bingham (13, p. 109) and also at Messina as noted below.

Covellite-tenorite is not a common association but melaconite derived from oxidation of chalcocite is "invariably accompanied by covellite" at Messina (87).

Cuprite-tenorite. Cuprite at Tintic is "always intimately associated with melaconite into which it merges by insensible degrees" (93, p. 701). In one occurrence there it results from oxidation of enargite in the sequence: enargite, olivenite, malachite, malaconite, cuprite. Conversely cuprite is surrounded by copper pitch ore at Chuquicamata, Chile (3, p. 708). At Mackay, Idaho (94) bunches of cuprite are "invariably" surrounded by a layer of tenorite and contain specks of native copper.

Association Not Observed.—Covellite-cuprite would be precluded by chalcocite-tenorite, which seems the more probable alternative, although there is not much information regarding oxidation products of covellite.

Summary: Cu-S-O.—

Observed Associations	*Inferred Three-Phase Fields*
Cu-cup	Cu-cc-cup
cc-cup	cc-cup-to
cc-to	cc-cv-to
cv-to	

TERNARY SYSTEM Cu-Fe-O (FIG. 5, LOWER)

Minerals.—No three-component mineral phases exist in this system except delafossite, $CuFeO_2$ whose associations are not well-known but are apparently similar to those of tenorite.

Observed Associations.—Native copper-hematite is not a characteristic association in hypogene ores; in fact native copper deposition is accompanied by reduction of ferric oxides and deposition of ferrous minerals (but not magnetite) (21). In oxidized ores, however, native copper is commonly associated with "limonite" (whether hematite or goethite is not usually determined) in many localities (68, p. 473, 75, p. 326, and 81, p. 64).

Cuprite-Hematite.—Cuprite and "limonite" are very commonly associated in oxidized ores, often with native copper, as noted above.

An alternative to this assemblage, tenorite-magnetite, is not reported in nature. Although Park (67) found CuO and Fe_3O_4 together in artificial products made at 160° to 300° C in open systems with a gas phase, it is significant that, where these two compounds were associated, others were present as well and the number of solid phases exceeded the number of components, showing that equilibrium had not been attained.

Tenorite-hematite, or tenorite-"limonite" is an association not often specifically reported, although there appears to be no alternative to such a tie-line.

Associations Not Observed.—Native copper-magnetite has been observed in converter slags where metallic copper occurs as spheroids within spheroids of chalcocite surrounded by glass that contains octahedral crystals of magnetite (27, Fig. 204). Whether or not this indicates compatibility, the association

Cu-magnetite is not reported in natural ores, although no tie-lines are evident that would preclude it. In oxidized ores the activity of oxygen is apparently too high for stability of magnetite.

Cuprite-magnetite would be precluded by a tie-line native copper-hematite.

Summary: Cu-Fe-O.—

Observed Associations	*Three-Phase Fields*
Cu-hem	Cu-cup-hem
cup-hem	cup-to-hem
to-hem	

QUATERNARY SYSTEM Cu-Fe-S-O (FIG. 5)

Minerals.—As no mineral containing all four components is known the mineral phases are those of the four ternary systems.

Observed Associations.—In primary ores, associations involving all four components are those in which magnetite or hematite, or both, occur with copper-iron sulfides. In oxidized or partly oxidized ores, the copper oxides cuprite and tenorite appear but as the geometrical relations of the phase diagram would preclude their stability with any of the copper-iron sulfides in the presence of hematite they would not be expected among four-component assemblages.

Apart from assemblages already discussed under the ternary systems, the following two-phase associations in the quaternary system have been observed:

Magnetite occurs quite commonly with *chalcopyrite*. It occasionally appears in contact with *bornite* as at Engels, Cal. (34, plate 4). Although textures suggest that magnetite is decidedly the earlier of the two, no chemical relations are in evidence that would preclude a tie-line magnetite-bornite.

Magnetite-cubanite occur in the same ores at Flin Flon (14) Fierro, New Mexico and Parry Sound, Ont. (76, pp. 270–277). Descriptions of textural relations are sparse but no reason is evident why magnetite should not be compatible with cubanite or at least with cubanite-chalcopyrite solid solution.

Hematite occurs with *chalcopyrite* and less commonly with *bornite* or chalcocite. Thus at Virgilina, Va. (52) chalcocite and minor chalcopyrite occur with specularite and at Messina (87) hematite plates are rounded by bornite and chalcocite.

Associations Not Observed.—Chalcocite-magnetite are rarely if ever found together. They would be precluded by the ternary assemblage native copper-bornite-hematite which, however, is also rare or lacking.

Covellite-magnetite is precluded by any of the following three-phase assemblages: bornite-chalcopyrite-hematite, bornite-pyrite-hematite or chalcocite-pyrite-hematite.

Cubanite-hematite is precluded by the common assemblage chalcopyrite-magnetite-pyrite.

Bornite-cuprite is precluded by chalcocite-hematite:

$$2\ \text{bn} + 3\ \text{cp} = 8\ \text{cc} + \text{hem}$$

Chalcocite-pyrite-magnetite, a three-phase assemblage, is precluded by the join bornite-hematite,[7] similarly: *bornite-pyrite-magnetite* is precluded by chalcopyrite-hematite.[7] Pyrite and bornite can occur together, of course, in the absence of magnetite (Fig. 6).

Four-Phase Fields.—From the relationships discussed it is possible to infer certain three-phase fields represented by triangles whose corners are mineral phases on different ternary diagrams, i.e., "tie-planes" within the tetrahedral model. These are listed below under Summary. (In this listing digenite is omitted because its relations with oxides are not well-known; no doubt in some assemblages, "digenite" should be substituted for "chalcocite.")

These triangular tie planes divide the space within the tetrahedral model into four-phase fields, each having the shape of a distorted tetrahedron or sphenoid. Some of these are shown in Figure 6. It is of special interest that, if this configuration is correct, bornite and pyrite cannot be stable together along with magnetite although they can coexist with hematite.

Full relationships within the tetrahedron are not easy to show on paper but Figure 7a is a section parallel to the Cu-Fe-S base at the composition 10 atomic percent of oxygen. Here the triangular and quadrilateral fields represent possible four-phase assemblages. For other percentages of oxygen up to the composition of cuprite (33⅓%) the assemblages would be the same although the fields would vary in shape.

The assemblages inferred for conditions of supergene oxidation (Fig. 7b) are listed separately as it is assumed that under these conditions the tie-lines covellite-bornite and covellite-chalcopyrite are valid instead of chalcocite-pyrite.

Summary: Cu-Fe-S-O.—

Inferred Four-Component Tie-Lines

cc-hem	cp-hem
cv-hem	cp-mg
bn-hem	cn-mg
bn-mg	

Four-Phase Fields

(Hypogene conditions)

cc-cv-py-hem	cp-py-mg-hem
cc-bn-py-hem	cp-po-py-mg
bn-cp-py-hem	cp-po-cn-mg
bn-cp-mg-hem	

Four-Phase Fields

(Supergene conditions)
hem with:

Cu-cc-cup	cc-cv-bn
cc-cup-to	cv-bn-cp
cc-cv-to	cv-cp-py

Inferred Three-Phase Tie-Planes

cc-py-hem	cp-py-hem
cv-cc-hem	cp-py-mg
cv-py-hem	cp-po-mg
bn-py-hem	cp-cn-po
bn-cp-hem	po-py-mg
bn-hem-mg	py-mg-hem

Inferred Three-Phase Tie-Planes

(Supergene conditions)
hem with:

cc-cv	cv-bn	bn-cp
cc-bn	cv-cp	cc-cup
		cc-to

[7] Priestly Toulmin and Ulrich Peterson in private correspondence called attention to these relationships as a result of studies on a Chilean deposit.

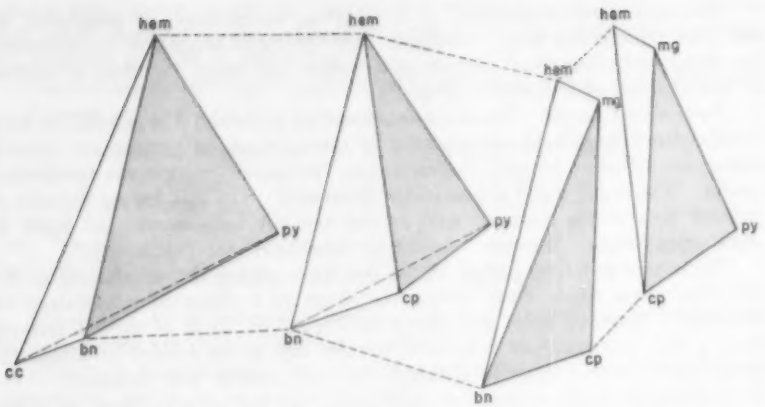

FIG. 6. Inferred four-phase fields in part of the system Cu-Fe-S-O (not to scale).

DISCUSSION

That the phase diagrams proposed here have the form of isothermal diagrams but are not labelled as to temperature immediately raises the question: What temperature do they represent?, a question whose answer can only be inferred. In some fields they are apparently valid both for temperature of deposition and for room temperature. In others they may represent either one or the other but not both.

Some minerals that crystallized at high temperatures certainly undergo change; high temperature phases may invert on cooling as in the case of chalcocite. Solid solutions unmix in varying degree. Thus chalcopyrite solid solution if rich in iron changes to an intergrowth of chalcopyrite and cubanite.

But chemical reaction between one mineral and another is a different matter and it does not follow that it always, or even commonly, has taken place to the extent that the minerals we see in contact with each other in the mine or museum are compatible at low temperature. For example among sulfides rich in copper we find in one place chalcopyrite-pyrite, in another digenite-chalcopyrite and in still another covellite-bornite. Obviously not all of these pairs can be stable at low temperature, yet they have not reacted. Undeniably, post depositional reaction can take place, but the geological and chemical evidence points to far more tendency to such reaction at high temperature and in the presence of fluid than in the cool dry state. That complete equilibrium is rarely attained is evident from the fact that a hand specimen or even a microscopic field often shows more phases than the phase rule permits.

Sequence of Deposition.—The fact that post-depositional reactions are possible, however, raises further questions regarding the interpretation of textures. To what extent do replacement textures and other generally ac-

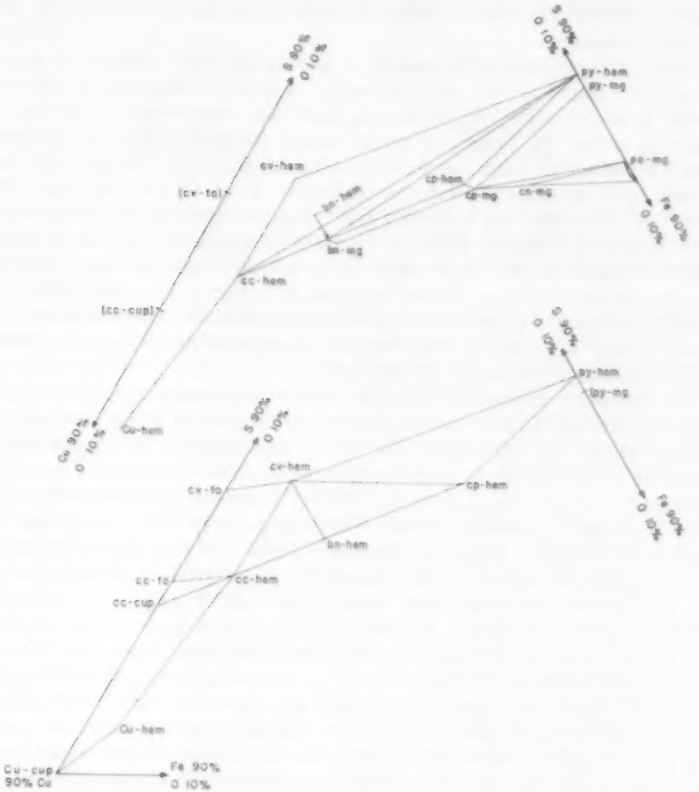

FIG. 7. Section through the tetrahedral model at composition 10% O. Upper: Mesothermal conditions. Lower: Supergene conditions.

cepted criteria of sequence record the history of actual deposition and to what extent are they modified by readjustments after active deposition has ceased? In particular, if the orebody is still hot and fluids are still present, reactions can continue. This question is much in need of further investigation.

In proposing phase diagrams for several ternary systems McKinstry and Kennedy (60) pointed out that in the system Cu-Fe-S the "usual sequence" or "general mineral succession" as listed by Lindgren (56) and by Newhouse (64) is identical, except for the reversal of pyrite and pyrrhotite, with the order in which minerals would appear and disappear if a sequence of assemblages, starting with chalcopyrite-pyrrhotite, became progressively richer in sulfur without change in the ratio of copper to iron. By reference to typical curves of equilibrium for reactions involving a volatile phase, they showed that such a succession of assemblages could result either from an in-

crease in partial pressure of sulfur or from a decline in temperature during or after deposition.

While this suggestion is capable of explaining many aspects of sequence it was not offered as the sole influence. Applied to the copper-iron sulfur system it would imply that in passing from any assemblage to the one next higher in sulfur the amount of pyrite would increase. Such an increase is indeed indicated at Butte, at least in some stages, where bright new pyrite crystals have developed in vugs in chalcocite; also at Cerro de Pasco where Lacy (51) describes no less than six types and generations of pyrite. In many localities, however, pyrite is replaced progressively by copper-bearing sulfides, a sequence that could come about only through increase of the ratio of copper to iron with or without increase in sulfur in the assemblage. The offhand explanation would be change in composition of solutions but the alternative, change in solubility with change in temperature or in other environmental conditions remains to be explored.

The tendency toward increasingly sulfur-rich assemblages, as deposition proceeds, although clearly a strong influence, does not as a rule continue to its ultimate result. If adequate sulfur were still available as temperature declined, all simple copper sulfide deposits would now consist of a mixture of pyrite and covellite, the assemblage that is stable below about 400° C and with sulfur vapor pressure as low as 0.05 atmosphere. Obviously this association is not common and even where it is found it is confined to only a small portion of the ore deposit. Even chalcocite and digenite are much less common as primary minerals than chalcopyrite and bornite. A partial explanation, of course, is that sulfide minerals, once deposited, are sealed off from further reaction with liquids and vapors unless they become re-fractured. But the very common persistence of low-sulfur assemblages and complete absence of covellite in most chalcopyrite deposits must mean that sulfurous fluids escaped or were used up soon after deposition ceased. In fact minerals of a late generation rather commonly show a reversal of the trend toward increasing sulfur content. At Butte late chalcocite replaces covellite, and tennanite replaces the higher-sulfur mineral enargite in what Linn (57) has aptly termed a retrograde sequence. This could result if late increments of orebearing solution were low in sulfur or if late-stage reactions occurred while the ore was still hot. Park (67) showed that covellite is changed to "chalcocite" in an atmosphere of steam at as low a temperature as 110° C.

An extreme example of such a reaction is found where the ore has been reheated, as by a post-ore dike. Thus at Butte, near intrusive dikes, chalcocite-pyrite ore has been converted to bornite-chalcopyrite (72) and at the Eustice Mine, Quebec (88) chalcopyrite-pyrite ore is converted to chalcopyrite-cubanite-pyrrhotite with loss of sulfur.

In the quaternary system, containing oxygen, the trend of the sequence usually observed in primary deposits is toward assemblages progressively richer in sulfur and poorer in oxygen with or without an increase in the ratio of copper to iron. Most deposits containing primary iron oxides belong either to a high-iron sequence characterized by pyrrhotite among the early minerals or a high copper sequence characterized by bornite. Thus the fol-

lowing alternative succession of (two or) three phase assemblages can be recognized:

High Fe : Cu	*Lower Fe : Cu*
mg-po	
mg-po-cp	mg-bn-cp
mg-cp-py	hem-bn-cp
hem-cp-py	hem-bn-py
hem-py-bn	

At some localities the beginning of the sequence is reversed notably in the appearance of pyrite before pyrrhotite. Ultimately hematite is progressively eliminated by sulfidization but in some districts it persists at the outer margin of mineralization.

Where pyrrhotite has survived to a late stage the tendency to elimination of oxygen from the system may be reversed, presumably in the presence of water and/or CO_2. Thus at Kaveltorp, Sweden (65) pyrrhotite and cubanite are cut by marcasite-magnetite veinlets and at Renison Bell, Tasmania (26, p. 116) pyrrhotite has broken down to form fine-grained magnetite-marcasite or magnetite-pyrite intergrowths. These reactions could occur with simple addition of oxygen; whether the sulfur content is actually increased, decreased or unchanged is not determined.

Minerals as Thermometers.—Disregarding exceptions and local reversals the general tendency to form assemblages progressively richer in sulfur at the expense not only of low-sulfur sulfides but also of magnetite and ultimately of hematite calls for a new look at the conventional concept of "high temperature minerals." Magnetite and (except for certain polymorphic phases) pyrrhotite are not in themselves high-temperature minerals for both can form and be stable at low temperature. They are typical of assemblages formed at high temperatures because at high temperatures pyrite would not be stable. At lower temperatures and with adequate chemical potential of sulfur they would be converted to pyrite-bearing assemblages. They are preserved where either (a) ore deposition ceased while the temperature was still high, (b) insufficient sulfur was available for more complete sulfidization or (c) they were isolated from the attack of ore-bringing fluids. Thus in attempting to use such minerals as thermometers one must consider not the individual minerals but the assemblages in which they occur.

ACKNOWLEDGMENTS

To Gunnar Kullerud, Eugene Roseboom and Robert M. Garrels I am extremely grateful for information and not only constructive but also properly destructive criticism of an earlier draft of this paper. They are in no way to be held responsible for errors or heresies in the present version. In preparing the section on the system Cu-Fe-S an unpublished review prepared by Ulrich Petersen in 1956 has been very useful.

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CAMBRIDGE, MASS.,
Dec. 23, 1958

APPENDIX

List of abbreviations used in figures and equations. Cf. Chace (22).

bn	bornite	Cu_5FeS_4	Fe	iron	Fe
cc	chalcocite	Cu_2S	hem	hematite	Fe_2O_3
cn	cubanite	$CuFe_2S_3$	mg	magnetite	Fe_3O_4
cp	chalcopyrite	$CuFeS_2$	ms	marcasite	FeS_2
cv	covellite	CuS	po	pyrrhotite	$Fe_{1-x}S$
Cu	copper (native)	Cu	S	sulfur	S
cup	cuprite	Cu_2S	to	tenorite	CuO
di	digenite	Cu_9S_5			

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Economic Geology
Vol. 54, 1959, pp. 1002–1034

ORE GENESIS IN THE NAICA DISTRICT, CHIHUAHUA, MEXICO

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CONTENTS

PAGE
Abstract 1002
Introduction 1003
Geography 1003
History 1004
Previous geologic work and present study 1005
Acknowledgments 1005
Stratigraphy 1006
Igneous rocks 1007
Metamorphic rocks 1007
Marble 1007
Skarn 1008
Wollastonite-garnet-vesuvianite (idocrase) zone 1009
Hedenbergite-quartz-calcite zone 1009
Structure 1010
Regional structure 1010
Structure in mine area 1010
Northwest fractures 1013
Northeast fractures 1014
Ore deposits 1015
Mantos 1016
Silicate-sulfide mantos 1016
General features 1016
Sulfide mineralization 1017
Crystalline calcite-sulfide mantos ("copper mantos") 1019
Genesis of the mantos 1020
Chimneys 1024
Sulfide-silicate chimneys 1024
Massive sulfide chimneys 1025
Genesis of the chimneys 1027
Genesis of the primary ores of the Naica district 1028
Oxidation 1032
References 1033

ABSTRACT

In the Naica mining district of north-central Mexico, pyrometasomatic and mesothermal replacement bodies of basemetal sulfides with minor amounts of silver and gold occur in a thick sequence of locally marmorized Cretaceous limestone. The only igneous rocks known in the Sierra de Naica, consisting of thin, discontinuous dikes and sills of very fine-grained

quartz and feldspar, have themselves been altered and partly replaced during ore emplacement.

Ore emplacement in the district was controlled by dikes and sills, and steeply dipping NW and NE fractures. Movement took place on faults belonging to both of these fracture sets before, during, and after the period of mineralization. Two structural types of orebody are exposed—gently dipping silicate-sulfide sheets or "mantos," and steeply plunging chimneys of sulfide ore with or without minor amounts of silicates, localized along steep NE or NW faults. The main manto consists of a central zone with wollastonite, grossularite, and vesuvianite (idocrase), and minor scheelite. This zone grades laterally into ore containing manganhedenbergite, quartz, and calcite, that was deposited in cooler ground adjacent to the central conduit. The fluids that deposited these marginal zones were depleted in Al, W, and Ag, and relatively enriched in Fe by the deposition of silicates and sulfides in the central zone of the orebody.

The silicates and sulfides were introduced into the manto by a single fluid that did not change in composition during the course of formation of this orebody. Silicates were deposited first, followed by sulfides that crystallized at temperatures on the order of 500°–550° C. The mantos were cut by silicate-bearing chimneys of sulfide ore that were in turn succeeded by mesothermal massive sulfide ore during the last stages of mineralization in the district. Most of the mesothermal ore appears to have been deposited at the same temperature and pressure as the earlier pyrometasomatic ore, suggesting that in this instance, the difference between the two types of ore is due to progressive changes with time in the composition of the ore-forming fluid, rather than to changes in the physical conditions of deposition. The silica, aluminum, magnesium, tungsten, and silver content of the fluid decreased relative to the content of lead, zinc, iron, and sulfur. In addition, the amount of iron carried by the fluid increased markedly with respect to lead and zinc during the course of mineralization in the district. While the oxidation state of the fluid as a whole remained nearly constant with time, it did change, due solely to the drop in temperature, during the course of crystallization within each successive orebody. The inferred changes in the mineralizing fluid with time are virtually identical to the changes in the mantos produced by the progressive reaction of the fluid with limestone.

INTRODUCTION

Geography.—The Naica mining district is in the south-central part of the state of Chihuahua, Mexico, about 100 km southeast of the city of Chihuahua, and 25 km southwest of Concho Station on the National Railway and Pan-American Highway (Fig. 1).

The district lies within the physiographic province of Mesa del Norte (13), an area characterized by elongate mountain ranges separated by broad basins or "bolsons." The ranges make up only a small portion of the total area of the province, and generally occur as fault blocks, or, as at Naica, as anticlinal mountains complicated by smaller-scale folding and faulting. The town and mines of Naica are on the northeast flank of a small range of low mountains that rises about 400 m above the broad alluvial valleys that border it on the east, south, and west. The entire range is about 12 km long, and roughly 7 km wide at its widest point. The principal mine portal, the Toledo adit (0 level), is at an elevation of 1,385 meters above sea level.

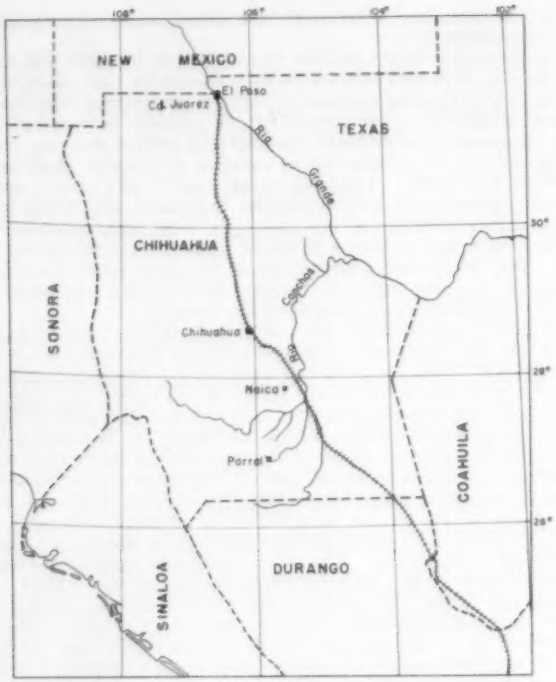

FIG. 1. Index map.

History.—According to Almada (1, p. 606) the first claim on the Naica district was filed in 1794, but the mines were not developed on a large scale until a railway line between Concho and Naica was built at the end of the last century. By 1911, when political unrest temporarily suspended mining activity, operations had been carried on down to the water table (about 130 m below the 0-meter level). In 1950, the Fresnillo Company leased the Naica mine from Minas de Naica, S. A., and erected a 400-ton mill for concentrating the sulfide ores found below the water table. The water level in the mine was lowered through the use of submersible pumps installed in 24-inch churn drill holes drilled from the 120-m level, and mining was carried on down to the 190-m level. In 1956, the Fresnillo Co. acquired the adjacent Gibraltar mine, and at present is the only company operating in the district.[1] The mill was enlarged to the present capacity of 1,200 tons per day, and the pumping rate was increased from about 3,500 to about 7,000 gallons per

[1] In the following discussion, the term "Naica mine" will refer to the entire property operated by the Fresnillo Company.

minute. The 240-m level was developed, and preparations for the development of a 290-m level are under way at the present time.

Previous Geologic Work and Present Study.—Several brief reports have been published on the Naica district, most of which are chiefly concerned with the engineering aspects, and present no more than brief sketches of the geological setting of the ore deposits. Authors of these articles and notes include Lambert (27), Paredes (35), Prescott (36), Horcasitas (17), and Gonzalez-Reyna (14). Of these, the note by Prescott is the most complete from a geological viewpoint. In addition to these general accounts, papers by Degoutin (8), Foshag (12), and Stewart (39) describe the occurrence of large (2 m long) crystals of selenite found in caves a few meters above the water table. More recently, papers on the district by Wilson (42) and by Bassett (4) have been presented in connection with the Twentieth International Geological Congress, held in Mexico in 1956. In addition to these accounts, I have had access to various company reports, diamond drill logs, geologic maps, and assay maps.

This paper is an abridgment of a doctoral dissertation submitted to the School of Mineral Sciences of Stanford University. It is based on the results of seven months of work at Naica, together with several months of laboratory study at Stanford.

Work at Naica consisted mainly of mapping and sampling mineralogic and metamorphic zones within and around the various orebodies in the district. Data from this mapping program were superimposed on the geologic maps of the mine workings prepared by Dr. I. F. Wilson, the resident geologist at Naica.

In all, there are over 20 kilometers of open workings in the mine, and in addition to the workings, core from an extensive diamond drilling program was available for study. During the course of the work, Wilson's ore units were split down into several mappable phases, and the relation of these phases to one another was studied in detail, in the hope that these relationships would provide a means of determining changes in physical and chemical conditions during the course of ore deposition. Although much of this work rests on the foundation supplied by Wilson's careful and accurate mapping, I alone remain responsible for errors of fact or interpretation that may be present in this paper.

Acknowledgments.—This study has benefited from the assistance, advice, and encouragement of many people. My father initially proposed the problem. The assistance of Mr. H. F. Keller and many others at Naica greatly furthered the progress of the field work. In particular, the advice and constructive criticism offered by Dr. I. F. Wilson was of great value. Without the suggestions and encouragement offered by Professors C. F. Park, Jr., K. B. Krauskopf, C. O. Hutton, and Adolph Knopf of Stanford University, the original paper would never have been written. However inadequate these formal words may seem, I wish to express my sincere gratitude and deep indebtedness to each of these men.

STRATIGRAPHY

The Sierra de Naïca is composed predominantly of Lower Cretaceous limestones, with a single thin shale member near the top of the range. The known ore deposits are confined to a thick limestone formation that has been correlated with the Lower Cretaceous Aurora limestone of the lower Conchos valley (42, p. 66). In the mine area, the Aurora limestone has been divided into three poorly defined members, partly on the basis of differences in behavior during the metamorphism accompanying ore deposition. Time did not permit a detailed study of surrounding non-mineralized areas, so the unmetamorphosed equivalents of these units are not known. Since the behavior of the Aurora limestone during metamorphism depends not only on the original nature of the rock, but also on its proximity to centers of mineralization, the three "members" are not map units except in a very general sense.

1) *Lower member.*—This unit consists of at least 330 m of medium to dark gray limestone, marmorized in part and containing scattered needles of wollastonite. Bedding is obscure, but may have been obliterated during metamorphism and recrystallization. This member does not crop out in the immediate mine area, and is found only in the lower mine workings and in deep diamond drill holes. Its base is not known. On the basis of microfossils from argillaceous beds, Fries (42, p. 68) suggests that at least part of the member might be of Aptian age.

2) *Middle member.*—This unit, exposed in mine workings and on the surface, consists of about 340 m of white to light gray, fine-grained, slightly marmorized limestone. A few bands of dark gray marble with wollastonite needles occur in the member, and a few chert nodules (now converted to wollastonite) have been found in the lower part of the unit. Bedding is generally well preserved, even where the original limestone has been entirely converted to white marble.

Most of the known ore deposits are found in this "member," but this is probably due partly to the fact that in the immediate vicinity of the larger orebodies, gray marble typical of the lower "member" of the Aurora has been converted to white granular marble, presumably by metamorphism connected with ore emplacement.

3) *Upper member.*—This unit consists of about 150 m of medium to thick-bedded, light to medium gray, fine-grained limestone with nodules and lenses of black chert. The limestone contains rudistid banks, gastropods, and foraminifera. On the basis of the foraminifera, Humphrey and Fries (42, p. 66) have assigned this member of the Aurora limestone to the Albian.

Conformably overlying the Aurora limestone are thirty meters or so of thin-bedded yellowish-gray marly shale. The basal portion of the section exposed northwest of the principal mine area consists of fissile, carbonaceous shale. The upper portion of this section is a highly fossiliferous marl containing a diagnostic upper Albian fauna (42, p. 68).

At least two more limestone units conformably overlie the shale. The lower consists of about 30 m of thick-bedded, light gray limestone with small

corals, and the upper consists of at least 100 m of massive light gray limestone that forms cliffs near the top of the range. At least part of this limestone is of Cenomanian age (42, p. 68).

Tertiary volcanic rocks cap low hills west and northeast of the Sierra de Naica. The oldest volcanic rocks exposed are fine-grained porphyritic dacites with interbedded pyroclastic material. Although not worked out in detail, the section appears to be at least 100 m thick. These rocks may once have capped the Sierra de Naica, but if so, have been completely stripped away by erosion.

Recent olivine basalt unconformably overlies the sequence of felsic volcanics. These rocks form low cones and short flows that are in part younger than the thick blanket of alluvium that underlies the valley north and east of Naica.

IGNEOUS ROCKS

The only igneous rocks exposed in the Sierra de Naica, either on surface or in the mine workings, occur as thin, discontinuous dikes and sills of aphanitic, light gray felsite. On surface, the rock weathers to a tan or reddish color, and small blocks show concentric red and yellow banding. The unaltered rock is so fine-grained that identification of the component minerals with a hand lens is impossible. Under the microscope, the principal minerals are seen to be quartz and allotriomorphic potash feldspar in highly variable proportions. Some sections apparently consist almost entirely of lath-shaped crystals of albite (42, p. 69), but none of these rocks were seen during this study. Since different phases of the rock cannot be distinguished in the field, all the fine-grained dikes and sills in the mine were mapped as "felsite." Where fresh or only moderately altered, the dikes and sills locally show flow banding parallel to the contacts between the felsite and the enclosing marble or limestone. It is interesting to note that these rocks closely resemble some of the intrusive felsites reported from the Yerington district (20, p. 13–16).

On the surface, several discontinuous lenticular dikes and sills crop out over the central mineralized area, and more extensive thin sills have been intruded into the top of the Aurora limestone a meter or so below the contact with the overlying shale. In many places, the effect of the felsite on the limestone has been so slight that the smell of hydrogen sulfide can be detected when the limestone a centimeter from the contact is struck with a hammer.

METAMORPHIC ROCKS

Two principal types of metamorphic rock are present in the Naica district. One of these is a calc-silicate skarn or tactite, and the other is the marble produced by the metamorphism of the Aurora limestone.

Marble

Most of the non-mineralized "country rock" in the mine area is dark gray to white marmorized limestone. A general picture of the distribution

of the marble was presented under stratigraphy, where it was emphasized that the behavior of the Aurora limestone during metamorphism was conditioned by distance from centers of mineralization, as well as by differences in composition or original texture.

Adjacent to an orebody, the normal white marble has been leached and recrystallized. The pronounced twinning characteristic of the calcite grains of the normal white marble has been destroyed, and the borders of the individual grains have been attacked and corroded. In addition, the calcite in these recrystallized areas is strongly fluorescent in shades of pink and red, whereas the normal white marble does not fluoresce under ultra-violet light. The fluorescence is apparently due to trace amounts of lead present in the recrystallized calcite, but not in the normal marble (38, 7). In summary, this evidence strongly suggests that the normal white and gray marble in the mine is due entirely to thermal recrystallization of the original limestone, unaided by fluids emanating from centers of mineralization.

The differences between white and gray marble are apparently due partly to temperature of metamorphism and partly to the original carbon content of the rock. During the bleaching of gray marble close to an orebody, the graphite dust that gives the rock its color was concentrated into small discrete grains, or was expelled from the rock altogether. Spectrographic analyses of the two types of marble and of the intercalated unaltered limestone fail to reveal any significant or consistent differences in the content of Mg, Si, Al, Fe, or Mn that might cause differences in behavior during metamorphism.

The lack of a significant difference is particularly puzzling in the occurrences of interbedded white marble and unaltered limestone in sharp contact with one another. Although space does not permit a detailed discussion of the reasoning involved, the difference in susceptibility to marmorization is attributed to differences in the permeability of the original limestone. The originally dense limestones have apparently resisted recrystallization, while the more permeable beds in the sequence have been altered to wollastonite-bearing marble.

Skarn

The principal bodies of sulfide-bearing calc-silicate rock or skarn in the Naica mine occur as gently dipping, relatively thin, extensive sheets or "mantos." These mantos are not similar in form to the gently dipping oval pipes commonly referred to as "mantos" in other Mexican districts (36, 32, p. 207), but are true blankets * of ore a few meters thick that extend laterally over areas of hundreds or even thousands of square meters. In general, these silicate-sulfide mantos dip gently west or southwest, and cut across the bedding of the enclosing limestone at low angles. In detail, however, they are somewhat irregular, and in places split or roll back on themselves (Fig. 3).

Several different mantos are exposed in the mine workings, one of which (the Azules-Navacoyan) constitutes one of the major orebodies of the mine. The Azules-Navacoyan is the largest and best exposed manto, and is the only one that clearly shows metamorphic zoning. It is four or five meters thick

* "Manto" means "blanket" in Spanish.

over most of its known extent, but toward the edge of the silicate sheet, a wedge of felsite occupies the core of the manto, and the mineable thickness decreases sharply. Locally, small veinlets branch from the hangingwall.

As may be seen from Figure 3, the Azules-Navacoyan manto consists of a high-temperature central zone characterized by the presence of grossularite garnet, vesuvianite and wollastonite that grades laterally into border zones containing hedenbergite, quartz and calcite. Both zones contain distinctive accessory minerals, as well as sulfides and fluorite. The two zones are gradational into one another over a distance of five or ten meters, and the distinction between the two rock types is further complicated by the fact that the manto appears to have spread laterally with time, so that early border phases have been overrun by later mineralization characteristic of the wollastonite-grossularite-vesuvianite zone.

Wollastonite-Garnet-Vesuvianite (Idocrase) Zone.—This zone, constituting the central portion of the manto, is characterized by the presence of coarsely crystalline white to pale pink manganiferous wollastonite, pale yellowish-green to flesh-colored anisotropic grossularite, and radial aggregates of acicular crystals of glassy, yellowish-green vesuvianite. Of these minerals, grossularite and vesuvianite make up between one half and two thirds of the total volume of the rock. Although wollastonite is one of the diagnostic minerals of the zone, it is not disseminated throughout the central portion of the manto, but is generally in pods and small masses of nearly pure material with individual crystals up to 30 cm long. Typically, these patches of coarse wollastonite are found along the hangingwall of the manto. Sulfides (galena, sphalerite, pyrite, chalcopyrite, and silver-bismuth sulfosalts), fluorite, and coarsely crystalline calcite are almost invariably present in minor amounts. Scheelite and adularia are characteristic accessory minerals of this zone, and some sections contain small amounts of an isotropic, brownish-yellow garnet (probably a member of the grossularite-andradite series), diopside, bustamite, chlorite, and late-stage quartz and anhydrite.

In one or two places in the mine, small felsite dikes have been partly replaced by massive grossularite containing scattered rosettes of vesuvianite, and the occasional altered and pyritized blocks of felsite found scattered through the central zone of the Azules-Navacoyan manto suggest the possibility that much of this manto may have originated through the replacement of a flat-lying felsite dike.

Hedenbergite-Quartz-Calcite Zone.—As may be seen from Figure 3, the wollastonite-grossularite-vesuvianite core of the Azules-Navacoyan manto is bordered by a zone characterized by gray-green, bladed to fibrous pyroxene (diopside-manganhedenbergite series), quartz, and fluorescent biaxial calcite. Yellowish-brown andraditic garnet is common in some parts of the zone, and sulfides and fluorite are present in most skarn of this type. Coarse-grained primary anhydrite, a small quantity of rhodochrosite, and traces of scheelite have been found. Chlorite is an alteration product of the garnet and pyroxene, and appears to have been formed at about the same time as the sulfides.

Quartz is associated with sulfides in both types of skarn, but in the

hedenbergite-quartz-calcite zone is present in considerable quantity, and appears to overlap the period of sulfide deposition (fig. 5). It replaces hedenbergite and calcite, and in places is veined by late-stage carbonate. Crystals of low-temperature quartz occur with crystals of calcite in vugs in sphalerite, as well as lining vugs that were later filled with sphalerite and primary anhydrite. Some of this quartz is pale purple in color.

The presence of quartz and calcite in skarn of this type, as contrasted with the appearance of wollastonite in the central portions of the manto, is taken to indicate that the hedenbergite-quartz-calcite zones of the manto represent the relatively low-temperature borders of the skarn as a whole. The two zones are not strictly contemporaneous, but it seems reasonable to assume that the hedenbergite-bearing zone was deposited immediately after the initial stages of the central core of the manto.

Along the northwestern edge of the manto, the silicates occur along the hanging- and footwalls of a felsite dike. At the edge of the skarn zone, the dike is essentially unaltered, but becomes progressively more altered and pyritized toward the wollastonite-grossularite-vesuvianite zone. No major bodies of felsite are exposed in the southwestern hedenbergite-quartz-calcite area, in the corner of the manto between the Torino and Gibraltar faults (Fig. 3).

STRUCTURE

Regional Structure

The small mountain group of which the Sierra de Naica is a part consists of a broad structural dome measuring about 12 by 7 km, elongated in a northwest-southeast direction. The dome has been complicated by smaller-scale folding, and by faulting, some of which apparently involves displacements of several hundred meters (3).

It has been suggested by Bassett (3, 4) and by Wilson (42, p. 70) that the domal form of the range is due to the presence in depth of a buried intrusive mass, presumably the source of both the felsite dikes and the fluids responsible for the mineralization at Naica. The deepest exploratory hole so far drilled in the mine reached the 620-m level, below the central mineralized area, but bottomed in essentially unaltered limestone, indicating that the inferred intrusive must lie some distance from this point.

Structure in the Mine Area

The Naica mine is on a secondary domal fold on the northeast flank of the major structure just described. Although no persistent "marker" beds exist in the accessible portions of the Aurora limestone, the fold is outlined by variations in the strike and dip of bedding throughout the mine (Fig. 2). The fold axis runs more or less through the center of the mine and plunges to the northeast. The crest of this structure in the lower levels of the mine roughly coincides with the highly fractured and mineralized ground between and adjacent to the Torino and Tehuacan faults.

At least two, and possibly three sets of faults can be distinguished in the

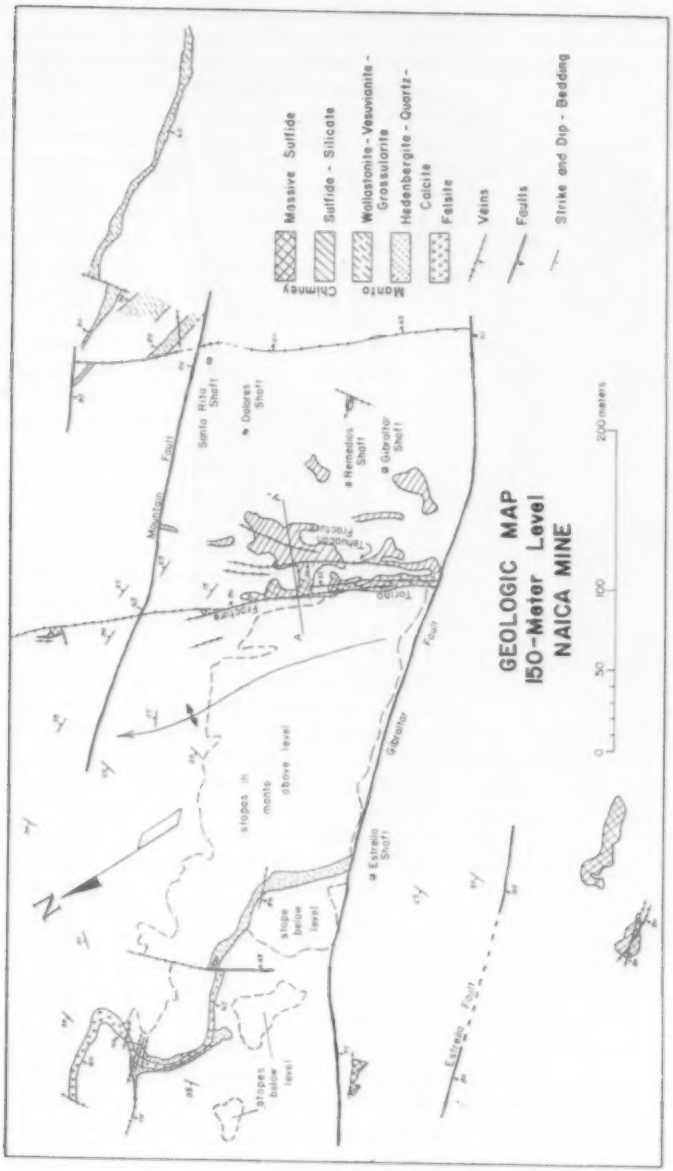

FIG. 2. Plan map of mine.

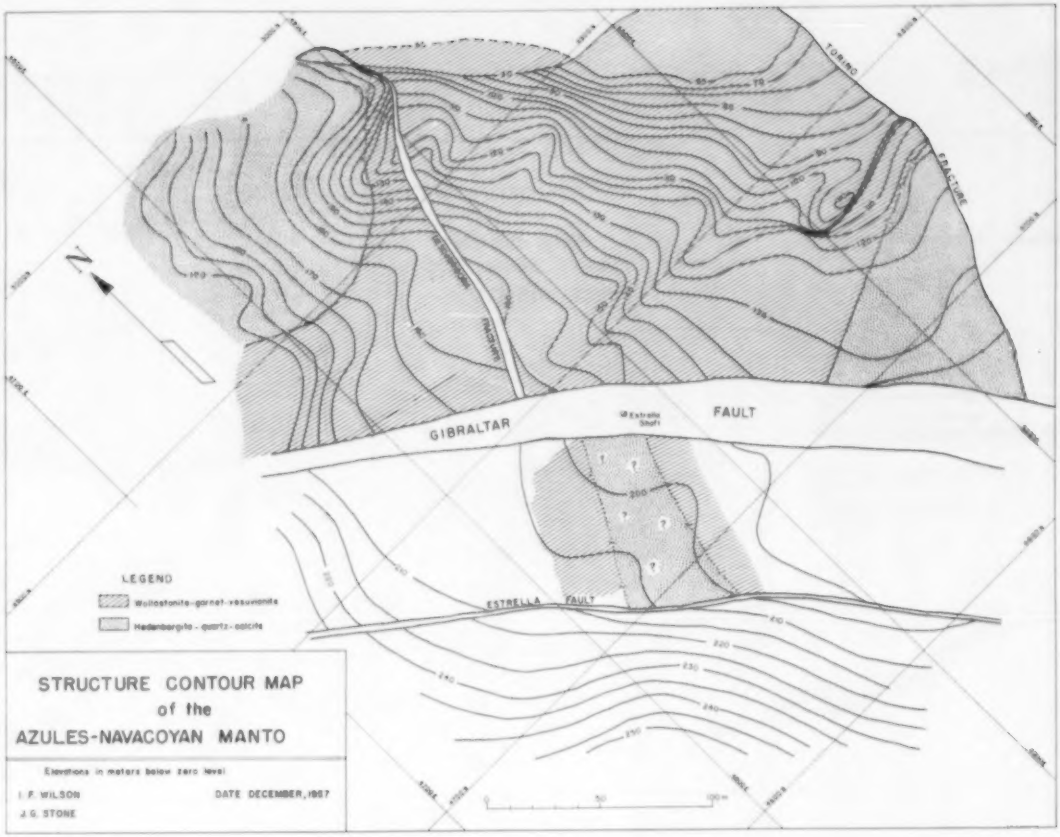

FIG. 3. Contour map of manto.

area, all of which seem to have been active during the entire period of mineralization. In addition, at least two of these pre- and intra-mineral fracture sets were active after the period of mineralization had come to a close.

The oldest of the three fracture sets is the most obscure, and is exemplified by a fracture or fractures that may have served to localize the felsite dikes and silicate mantos. Wilson (42, p. 71) postulates the existence of such a fracture, striking generally northwest, interrupted by short northeast stretches, and dipping gently toward the west. Above the 120-m level, the manto seems to split into two branches, and to roll back on itself (Fig. 3). These irregularities, and the fact that the manto in part follows the borders of a major felsite dike suggests that the fluids responsible for the formation of the manto may have followed the shattered hanging- and footwalls of an originally more extensive, tabular body of felsite that in places was intrusive more or less along the bedding of the limestone, and in places cut across it at high angles. Some movement must have taken place within or adjacent to the dike in order to shatter the brittle felsite and render it permeable enough to serve as a channelway for the fluids that replaced it (assuming for the moment that it was essentially continuous over most or all of the manto), but this fact does not necessarily indicate the presence of a through-going fault.

In summary, the first hypothesis demands the presence of a highly irregular low-angle fault that actually seems to roll back on itself; the second suggestion demands that the dike once extended over most of the area now occupied by the manto, but has been almost entirely replaced by garnet, vesuvianite, and other minerals.

Most of the well-defined fractures in the mine strike either N50°–60°W or N25°–35°E. These two fracture sets appear to have developed more or less concurrently, and movement took place on both sets after as well as during the main period of mineralization.

Northwest Fractures.—The earliest fractures of this set apparently developed more or less at the same time as the manto orebodies. In one place on the 150-m level, a shoot of high-grade manto ore has been formed at the intersection of the felsite dike and a group of pre-mineral northwest fractures. In this same area, a thin seam of sulfides along a bedding plane in the marble in the hangingwall of the main manto is cut by several small, parallel northwest fractures, all of which are almost certainly genetically related. However, some of the faults in this group cut and slightly displace the sulfides, but others in the group have themselves been mineralized by fluids that worked up into them during the formation of the bedding seam.

In several places in the Azules-Navacoyan manto, sulfides, locally accompanied by silicates, are found along small northwest veins that branch from the hangingwall of the main silicate-sulfide sheet. Some of these veins have been mined for considerable distances above the main body of the manto, but do not seem to extend through the manto and into the footwall. The fractures controlling these veins were therefore formed prior to, or possibly during, the early stages of the formation of the manto.

In general, these early northwest fractures occur as clusters or swarms of

discontinuous, nearly vertical, more or less parallel, mineralized faults with small displacements. The fractures appear both to cut and to be cut by northeast-trending faults and veins. Toward the end of the period of sulfide mineralization in the district, movement along northwest fractures apparently was concentrated in certain restricted zones, rather than spread out on small fractures over much of the mineralized area. Such a group of late northwest fractures served to localize the chimney of massive sulfide ore (characteristic of the late stages of ore deposition) southwest of the Estrella shaft (Fig. 2).

Post-mineral movement on northwest fractures took place mainly along the Estrella, Gibraltar, and Mountain faults. These three faults are normal faults with displacements of a few tens of meters. In addition to a dip-slip component, the rake of slickensides along minor post-mineral northwest fractures indicates that strike-slip movement took place on at least some of these faults.

Northeast Fractures.—Several fairly persistent northeast-trending fractures or fracture zones are exposed in the mine workings, two of which (the Torino and the Tehuacan) appear to have served as controls in the localization of the Torino-Tehuacan chimney, one of the largest orebodies in the mine. In general, the northeast fractures developed after the formation of the mantos, and more or less concurrently with the later intra-mineral northwest fractures.

The Tehuacan Fracture System appears to be one of the oldest northeast fracture zones in the mine. It dips 40°–50° NW and joins the steeply dipping Torino fracture zone slightly above the 190-m level, but is not present as a well-defined vein on or below this level. Blocks and horses of manto-type ore occur within the Tehuacan zone, indicating that the zone is younger than the mantos (Fig. 4). The total displacement on the zone has not been determined, due to the lack of reliable "markers." The Tehuacan fracture zone splits up and dies out approaching the Mountain and Gibraltar faults, and has been cut off by late movement on these two northwest fractures. This fracture zone seems to have localized the early sulfide-silicate phase of the Torino-Tehuacan chimney.

The Torino Fracture System is one of the most economically important vein systems in the mine. In the upper levels, above the water table, it yielded large tonnages of high-grade lead-silver ore, and below the 150-m level, it acted as one of the main controls in localizing the Torino-Tehuacan chimney. As may be seen from Figure 4, the dip of the Torino veins increases markedly with depth. On the 18-m level, the dip is 50°–55° SE, increasing to 70°–75° SE on the 150-m level. Near the junction with the Tehuacan vein system, the dip of the Torino passes through vertical, and on the 190-m level, veins and small fractures belonging to the Torino group dip at angles of 75°–80° NW. Below the 190-meter level, the original trace of the combined Torino and Tehuacan veins has been largely obliterated during the formation of the Torino-Tehuacan chimney, which below this level is a kidney-shaped pipe of ore some 80 m across.

The Torino is a reverse fault, with an apparent vertical displacement of

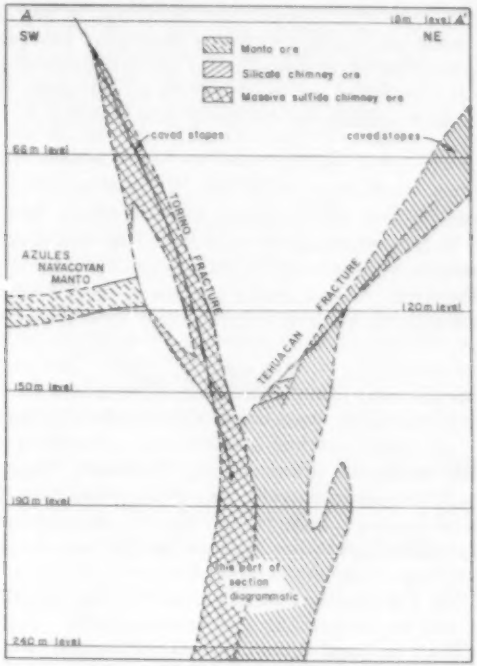

FIG. 4. A–A′ × section Torino-Tehuacan.

about 50 m. Although cut off by the Gibraltar fault, The Torino vein system appears not to have been offset by the post-mineral Mountain fault by any appreciable amount (Fig. 2).

Minor post-mineral fracturing has followed the line of weakness produced by mineralization along pre-mineral fractures of the Torino system. These post-mineral fractures controlled the circulation of water below the water table, and are generally bordered by oxides or filled with transported limonite for considerable distances below the level of the old water table. On the 66-m level, slickensided oxides along the Torino indicate that minor movement along this fracture zone continued for a considerable period of time after ore deposition had ceased. It is probable that most of this movement was caused by slumping of oxidized and leached portions of the vein below the 66-m level.

ORE DEPOSITS

The ore deposits of the Naica district are replacement bodies of base-metal sulfides with minor amounts of silver and gold in marmorized limestone and calc-silicate skarn. Two principal types of orebody can be distinguished:

1) mantos, and 2) chimneys. Small veins are common, both in the hangingwalls of the mantos and along northeast fractures, but generally are too narrow or discontinuous to be mineable for more than short distances. Ore emplacement was controlled by fractures (both northeast- and northwest-trending), dikes, and possibly by the domal fold trending through the center of the mine.

MANTOS

Two principal types of silicate manto occur at Naica, both of which have been mentioned in the section of the paper dealing with metamorphic rocks. In addition, several small mantos of coarse-grained (2–3 mm) granular calcite are known in the mine. These calcite mantos in places contain appreciable amounts of disseminated chalcopyrite, and for this reason are known as "copper mantos".

Silicate-Sulfide Mantos

General Features.—Both types of silicate manto contain sulfides as individual grains and small patches disseminated throughout the skarn, and as minor veinlets cutting the silicate sheet. Commonly there is an irregular layer of high-grade ore up to a couple of meters thick along the hangingwall and/or footwall of a manto, between the silicates and the enclosing marble. The tendency for sulfide orebodies to occur on the limestone side of silicate zones in pyrometasomatic ore deposits has been emphasized by Umpleby (41) who suggested that the observed zoning indicated that sulfide-bearing fluids were introduced into the system after the garnet and other silicates had formed, and that the sulfides replaced limestone in preference to the skarn. Other workers have concluded that the sulfides replace silicates as well as limestone (28, 37).

At Naica, there are objections to the hypothesis that the sulfides were deposited by a separate sulfide-bearing fluid introduced into the system during a separate "wave" of mineralization. The sulfide-rich zones along the tops and bottoms of the mantos show no indication of having originated as fissure veins localized by the silicate-marble contact. They faithfully follow the contact and do not cut across nor veer away from the silicate sheet as well-defined veins, even where the manto is highly irregular. There is apparently no preference for one wall of the manto over the other, and in many places sulfide-rich zones are equally developed along both contacts. In some areas, sulfides are absent along the contacts, but there is no obvious pattern or trend to the areas of high-grade ore that would indicate channelways followed by the hypothetical sulfide-bearing fluid. Not all patches and individual grains of sulfide in the body of the skarn are related to fractures, as would be expected if a late sulfide-bearing fluid had deposited all the sulfide minerals in and along the silicate sheet.

The Azules-Navacoyan manto has been cut off by the Torino vein and by the sulfide-silicate Torino-Tehuacan chimney. Both the sulfides and the silicates in the chimney differ significantly from the silicates and sulfides found in the manto. In addition, the pattern of metamorphic zoning in the

manto indicates that the source was more or less down the dip, and that the manto did not originate from the main chimney area. In this respect, the manto at Naica seems to differ from the gently plunging pipes or "mantos" of Santa Eulalia and other mining districts. These oval pipes almost invariably arise from a steeply plunging chimney of ore whose overall composition is very similar to the ore in the mantos (11, 36).

Sulfide Mineralization.—The sulfide minerals in the manto orebodies are predominantly pyrite, galena, and sphalerite, with lesser amounts of chalcopyrite, arsenopyrite, pyrrhotite, cosalite, matildite, and molybdenite. Gold is present in small amount (less than 1 gm/ton), presumably as native gold, but none was seen during the study. The sulfides vein and replace the associated silicates, and appear to have formed more or less contemporaneously with fluorite, adularia, and late-stage quartz and calcite (Fig. 5). Fluorite, quartz, and calcite are in part later than the sulfides, and occur as crystals in vugs in sulfide ore. Anhydrite seems to have formed largely after the period of sulfide deposition had come to a close, and has filled vugs in the skarn, some of which were originally coated with crystals of quartz and carbonates.

Slight differences can be recognized in the overall sulfide mineralogy of the two types of silicate ore (Fig. 6). The hedenbergite-quartz-calcite zone contains appreciably more iron (as pyrite) than does the wollastonite-garnet-vesuvianite skarn as a whole, and appears to have a somewhat higher average
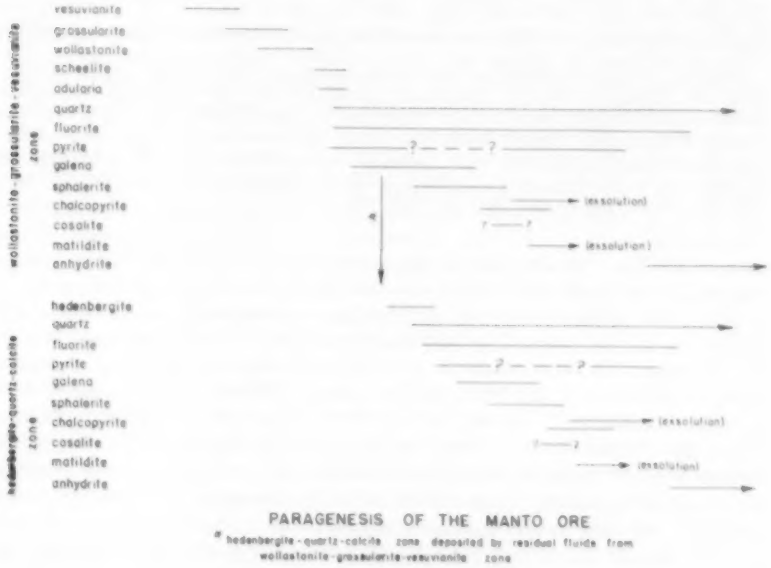
FIG. 5. Paragenesis of manto.

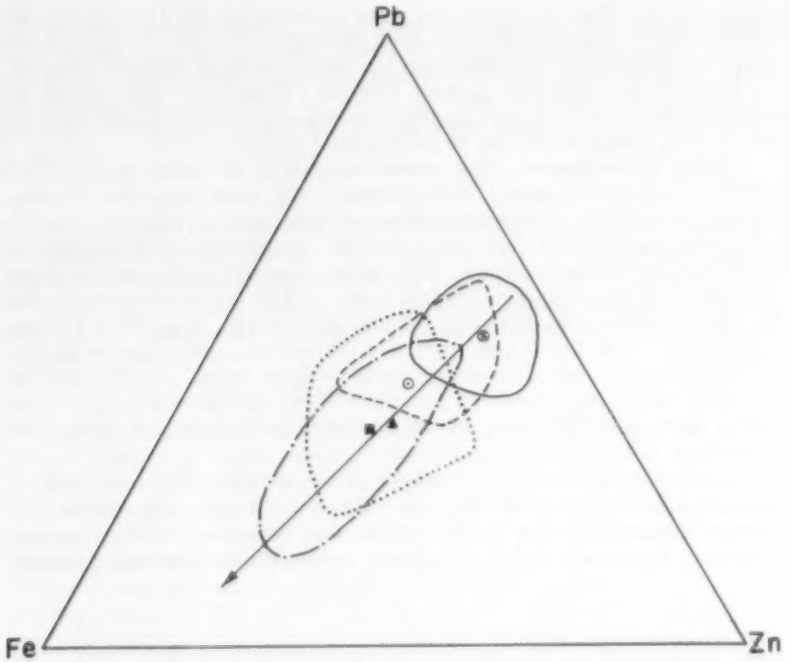

FIG. 6. Triangular diagram showing proportions of Fe (pyrite and/or pyrrhotite), Pb (galena), and Zn (sphalerite) in Naica ore. ⊗ = Average of wollastonite-vesuvianite-grossularite zone. Analyses fall inside solid line. ⊙ = Average of hedenbergite-quartz-calcite zone. Analyses fall inside dashed line. ▲ = Average of silicate chimney ore. Analyses fall inside dotted line. ■ = Average of massive sulfide chimney ore. Analyses fall inside dash-dot line. Arrow indicates shift in composition of ore-forming fluid with time.

ratio of Pb/Zn. On the other hand, the ratio of silver to lead in the central zone of the manto is about twice the ratio in the border zones (Table 1).

From the point of view of deciphering the conditions under which the Naica deposit was formed, sphalerite is probably the most important sulfide in the mine. In the mantos, it crystallized during the latter part of the paragenetic sequence, and veins and/or replaces silicates, scheelite, pyrite, and some of the galena. It is in turn replaced or overgrown by later galena, pyrite, quartz, and calcite. Much of the copper in this type of manto ore is present as small exsolved blebs of chalcopyrite concentrated near the borders of the sphalerite grains. Chalcopyrite is locally present in amounts that could not have been held in the associated sphalerite at high temperatures, and in these instances, seems to have crystallized at about the same time as, or slightly later than, the sphalerite.

TABLE 1

AG/PB RATIOS OF NAICA ORE

Manto Ore:	Wollastoniate-garnet-vesuvianite	77.5 gm/ton/%Pb
	Hedenbergite-quartz-calcite	33.5 gm/ton/%Pb
Chimney Ore:	Silicate-sulfide	25.2 gm/ton/%Pb
	Massive sulfide	22.6 gm/ton/%Pb

Kullerud (24) has shown experimentally that the amount of iron present in solid solution in sphalerite is a function of the temperature of formation, provided that excess iron is available at the time of formation. In the presence of excess sulfur, iron will form pyrite rather than enter into sphalerite, and the apparent temperature of formation as deduced from the iron content of the sphalerite will be too low. In much of the manto ore, sphalerite occurs with pyrite, suggesting that in these areas the system may not have been saturated with iron (with respect to sulfur) at the time the sphalerite was formed. In a few places, however, sphalerite is found that appears to have been in equilibrium with pyrrhotite or with pyrite *and* chalcopyrite at the time of formation. Since neither pyrrhotite nor chalcopyrite are sulfur-saturated minerals, their presence indicates that sulfur was not in excess during the deposition of the associated sphalerite. The pyrite-chalcopyrite assemblage must be used with caution as a sulfur "barometer," especially at temperatures above 300° C (2). From Table 2, it may be seen that sphalerite in both zones of the manto apparently was formed at about the same temperature. The figures given are taken from Kullerud (24), and are for sphalerite formed at atmospheric pressure, and are therefore minimum values, since an increase in pressure should decrease the amount of iron held in solid solution at any given temperature (24, p. 105–107). The crystals of low-quartz found in the mantos are generally somewhat younger than the associated sulfides, but in one or two places, euhedral crystals of low-quartz are enclosed in galena and chalcopyrite deposited after the formation of the crystals. Although these minerals could have been deposited after the period of sphalerite deposition, the fact that galena overlaps sphalerite in the paragenetic sequence suggests that the two minerals were formed at roughly similar temperatures. From this, and from work on pyrrhotite, associated with sphalerite in the Torino-Tehuacan chimney, it seems that the sphalerite "thermometer" may give results that are about 50° C too high in this temperature range (500–600° C), and the temperature of formation of the sphalerite in the mantos will therefore be taken as somewhere between 500° and 550° C.

Crystalline Calcite-Sulfide Mantos ("Copper Mantos").—Thin mantos consisting essentially of coarse crystalline marble and disseminated sulfides (principally chalcopyrite) occur in several places in the mine. They are generally associated with normal silicate-sulfide mantos, and appear to represent areas in which mineralizing fluids leaked away from the main mantos along beds of unusually coarse marble. A continuous gradation may be traced from mantos of nearly massive sulfides to beds of coarse non-fluorescent marble with widely scattered specks of chalcopyrite. These mantos are

TABLE 2

ANALYSES OF NAICA SPHALERITE

	Sample No.	wt% FeS	T of formation—1 atm (after Kullerud)*
Manto Ore			
Wollastonite zone:			
	225**	17.8 ± 0.3	570° C ± 10°
	223**†	17.6 ± 0.3	570° C + 10°
	207**	16.9 ± 0.3	550° C ± 10°
Hedenbergite zone:			
	189	18.5 + 0.3	590° C ± 10°
	131**	17.4 ± 0.3	570° C ± 10°
	204**	17.5 ± 0.3	570° C ± 10°
Chimney Ore			
Silicate-sulfide:			
	97	17.2 ± 0.3	550° C ± 10°
	137	18.3 ± 0.3	590° C ± 10°
	138	18.0 ± 0.3	580° C ± 10°
Massive sulfide:			
	60**	18.3 ± 0.3	590° C ± 10°
	62†	18.3 ± 0.3	590° C ± 10°
	227**	20.5 ± 0.3	630° C ± 10° (?)
	228**†	16.3 ± 0.3	540° C ± 10°

* These values may be about 50° C too high.
** Sample apparently in equilibrium with chalcopyrite and pyrite at time of formation.
† Sample apparently in equilibrium with pyrrhotite at time of formation.

appreciably higher in copper than is the normal ore from the silicate-sulfide mantos, and some contain traces of altered garnet and vesuvianite, associated with recrystallized, fluorescent calcite.

Genesis of the Mantos.—The manto orebodies at Naica are true pyrometasomatic deposits, consisting of metallic sulfides associated with calc-silicate minerals typical of contact-metasomatic aureoles. Although no major bodies of igneous rock are exposed in the Sierra de Naica, the immediate presence of an intrusive contact is not critical to the original definition of the term (30, p. 293), and for this reason the term "pyrometasomatic" is preferable to "contact metamorphic" or "contact metasomatic" in describing these particular orebodies. Knopf (21, p. 539) cites several examples of pyrometasomatic deposits localized by fissures as much as two miles from exposed igneous contacts.

The Naica mantos cut across the bedding of the enclosing marble, and cannot have originated from the recrystallization of an impure horizon in the original limestone, but must be due to the addition of large quantities of Si, Al, Mg, Fe, Pb, Zn, Mn, Ag, Cu, F_2 and S_2 into the calcium carbonate country rock. Most of the calcium in the skarn (in grossularite, vesuvianite, wollastonite, hedenbergite, and fluorite) presumably represents calcium derived from the replaced limestone. Probably small amounts of silica and

magnesium were also derived from the limestone, but the major portion of these elements must have been added from an external source, presumably an igneous body somewhat "at depth."

The pattern of metamorphic zoning in the Azules-Navacoyan manto conforms in a general way to the sequence of minerals developed during the progressive metamorphism of impure limestones (5, 40). At Naica, however, there is an important difference in the two zones that cannot be directly ascribed to variation in temperature of deposition, namely the distribution of aluminum.

Aluminum is a major element in the high-temperature wollastonite-bearing skarn, as an essential component of both grossularite and vesuvianite. In the hedenbergite-quartz-calcite zone, however, there are no major aluminum-bearing minerals. Some of the pyroxene in this zone contains as much as 5% Al_2O_3 and a little andradite is locally present, but by far the greatest amount of aluminum in the mantos is confined to high-temperature environments. There are two possible explanations to account for this distribution, both of which probably apply to these particular orebodies. It was suggested earlier in the paper that there is a possibility that at least part of the Azules-Navacoyan manto is the result of the replacement of a felsite dike. As would be expected, this replacement seems to be most extensive in the high-temperature portions of the mantos. Since the felsite dikes consist of a mixture of quartz and potash feldspar, most of the aluminum and much of the silica in this skarn could have been derived from replaced felsite. However, small veins of garnet bordered by wollastonite also occur in the mine, in areas where no felsite has been found. In these instances, it seems fairly certain that aluminum and silica were introduced into fractures in amounts such that the aluminum was used up in the formation of garnet before the supply of silica was exhausted. The surplus silica then reacted with the marble beyond the garnet to form wollastonite. By analogy, it seems possible that aluminum introduced into the central zone of the manto was almost entirely used up in the formation of grossularite and vesuvianite, leaving a residual fluid containing silica, iron, magnesium, and manganese (in addition to lead, zinc, sulfur, and fluorine), which deposited pyroxene, quartz, and sulfides in cooler ground adjacent to the central channelway.

When heated, grossularite from the mantos begins to lose its birefrigence at a temperature somewhere in the range of 700°–800° C. The maximum temperature at which the Naica grossularite could have formed will be taken as about 750° C. The period of grossularite deposition probably represents the period of highest temperatures during the formation of the manto as a whole, so that 750° C is a rough maximum temperature in the formation of the entire orebody. Presumably the hedenbergite-quartz-calcite skarn formed at a somewhat lower temperature than the wollastonite-bearing skarn, assuming that the partial pressure of CO_2 was roughly the same in both zones, but it is difficult to assign a definite figure for the maximum possible temperature. Since the sphalerite in this type of manto ore seems to have been deposited at a temperature between 500° and 550° C, and since sphalerite crystallized

late in the paragenetic sequence, it is safe to assume that the hedenbergite crystallized above 550° C. Since sphalerite was deposited toward the end of the paragenetic sequence, it seems likely that the first sulfides to form (pyrite and galena) actually began to crystallize at somewhat higher temperatures. At 743° C and a pressure of 180 psi, pyrite melts incongruently (26), so that this figure is a maximum for the entire period of sulfide deposition. In the absence of more precise data, 550° C is a reasonable guess as to the temperature at which the sulfides first began to crystallize.

The distribution of silver in the two zones of the manto suggests that deposition of sulfides in the central zone of the manto may have been contemporaneous with the early stages of silicate deposition in the hedenbergite-quartz-calcite zone. Cosalite and matildite are present in both zones of the manto, and since they both crystallized toward the end of the paragenetic sequence, the variation in the Ag/Pb ratio between the two zones is inferred to be due to variations in the amount of silver held in galena. In order to account for the difference in Ag/Pb ratios, it is necessary to assume that argentiferous galena began to crystallize in the central zone of the manto before the residual fluids moved into the cool ground adjacent to the central channelway. Similarly, tungsten was effectively removed from the mineralizing fluid by precipitation as scheelite. The fact that scheelite was formed fairly late in the paragenetic sequence of the wollastonite-bearing skarn, but still precipitated only in this zone rather than all through the skarn is taken to indicate that much of the hedenbergite-quartz-calcite skarn formed slightly after the central zone. This would be expected, of course, if the border zones were deposited by fluids impoverished in aluminum by the deposition of garnet and vesuvianite in the central zone.

At about the same time that sulfides first began to form in the central zone of the manto, the temperature had fallen and/or the partial pressure of CO_2 had risen to the point where wollastonite was no longer stable, and calcite and quartz were deposited together. Assuming a temperature of 550° C, the partial pressure of CO_2 necessary to prevent the reaction: $CaCO_3 + SiO_2 = CaCiO_3 + CO_2$ is about 135 atm (16). This reaction is very temperature-sensitive in the range of 500°–600° C, so that this figure should be taken with considerable caution. In view of the uncertainty of the sphalerite "thermometer," the CO_2 pressure at this stage in the formation of the manto will be estimated to have been about 100 atm. The total pressure on the system may, of course, have been a good deal more than this.

It has been shown that the sulfides were apparently introduced into the mantos at about the same time as the silicates, but crystallized somewhat later in the paragenetic sequence. Briefly, the evidence in support of the hypothesis is: 1) the high-grade sulfide zones along the top and bottom of the manto follow the borders of the silicate sheet and do not cut across it nor veer away from it, even where the manto is highly irregular; 2) the sulfide zones show no apparent relation to "feeder" fractures; 3) the pattern of sulfide mineralogy approximately corresponds to the pattern of mineral zoning observed in the silicates. A further line of evidence in support of the hypothesis is the fact

that the manto is cut by a sulfide-silicate chimney. As will be pointed out shortly, the sulfides in this chimney ore differ from manto sulfides. If the sulfides in both instances were introduced by a separate fluid after the formation of the silicates in their respective orebodies, it would be necessary to postulate four distinct pulses of mineralization.

The medium which introduced silicates and sulfides into what are now manto orebodies was presumably a high-temperature (550°–750° C) aqueous (?) fluid. Although well above the critical point of pure water (374° C), the fluid may or may not have been above its own critical point, depending largely on the amount of material held in solution. The density of the fluid would, in any event, be largely dependent on pressure. Unfortunately, it is difficult or impossible to arrive at an accurate figure for the total pressure acting on the system at the time of formation of the ore deposits. Bassett (3) has estimated a depth of burial of about 750 m at the time the deposits were formed, corresponding to a lithostatic pressure of about 185 atm. Since a replacement deposit demands that the system be at least partly open in order to allow removal of the replaced material, the total pressure on the system must be less than the simple weight of overburden. From this, it seems probable that the depth of burial may have been considerably greater than 750 m.

The material introduced into the mantos could have been present in the fluid in the vapor state (22) and/or held in solution in a compressed gas or supercritical aqueous fluid (34). The possible composition, and changes in composition with time of this fluid will be discussed later in the paper.

Vesuvianite was apparently the first mineral to form as the mineralizing fluid was introduced into relatively cool wallrock. The temperature seems to have risen somewhat with time, presumably due to the continued flow of material into the system. With the rise in temperature, the early volatile-rich vesuvianite was no longer stable, and was partly replaced by grossularite and wollastonite. With continued deposition of silicates, the solution channelways gradually sealed themselves off from further additions of fresh material, and the temperature in the mantos fell to the point where the residual solution began to precipitate sulfides and fluorite (Fig. 5). At about this same time, solutions depleted in aluminum, tungsten, silver, and possibly fluorine moving away from the central conduit deposited quartz and manganiferous pyroxene in the cooler ground adjacent to the main body of the manto. It is reasonable to suppose that the partial pressure of CO_2 rose rapidly during this stage of manto development, and that the formation of quartz and calcite during the late stages of mineralization reflects the fact that the system was gradually becoming more nearly closed, as well as the fact that the temperature was falling. There is nothing surprising in the fact that minor veinlets of sulfide cut the silicate sheet. It has been shown that minor fracturing was going on throughout the period of manto formation. As Emmons (10) pointed out, fracturing involves an increase in volume, so that a fracture in any body of rock will immediately be filled by any mobile material available (in this instance, by a sulfide-rich residual fluid).

The principal difficulty with the hypothesis that the sulfides were deposited from a residual fluid left over after the crystallization of silicates is the concentration of metal that must have been present in the original fluid. Neither simple vapor transport (22) nor simple solubility in aqueous solution (Czamanske, unpublished data) can account for the quantities of metal that the hypothesis demands, but in view of the somewhat meager knowledge concerning the behavior of solutions at high temperatures and pressures, the objection, although serious, is not damning.

CHIMNEYS

The most spectacular orebodies at Naica are steeply pitching pipes or chimneys of sulfides, with or without silicates, localized along steep northwest and northeast faults. The largest and most important chimney is the Torino-Tehuacan. The Torino and Tehuacan fault zones dip toward each other, and the orebodies controlled by these fracture systems merge to form a single pipe of high-grade sulfide ore some 80 by 50 m in horizontal section (Fig. 4). The Torino fracture cuts the Azules-Navacoyan manto, and faulted blocks of manto ore occur within the Torino and Tehuacan fault zones, proving that the chimney is younger than the mantos. In the following discussion of chimney ore, it must be borne in mind that the paragenetic sequence of minerals in the chimneys (Fig. 7) has nothing to do with the sequence in the mantos. The events of manto formation and chimney formation were separate in time, and are related only in that both orebodies were presumably derived from a common source.

In general, two types of chimney ore can be distinguished—massive sulfide ore, and heavy sulfide ore containing a minor amount of silicates. The two types are gradational, and the 5 percent silicate dividing line used in mapping is purely arbitrary.

Sulfide-Silicate Chimneys

The largest and best exposed silicate chimneys in the mine are related to the Tehuacan fracture, and for this reason, the discussion of this type of chimney will be essentially a description of these particular orebodies.

In many places on the 240-m level, the silicate ore shows a pronounced banding parallel to the edges of unreplaced blocks of marble, suggesting that the deposit originated through the replacement of a coarse breccia or shattered zone. The succession of bands of minerals varies from place to place, proving that there was no rigid sequence of introduction of mineral components into the deposit.

The silicate minerals found in chimney ore of this type include andradite garnet, pyroxene (both hedenbergite and diopside), tremolite, quartz, and a little wollastonite. The silicates have been veined and partly replaced by pyrite, galena, sphalerite, arsenopyrite, chalcopyrite, and pyrrhotite. Native gold is presumably present, and a little magnetite has been found on the 240-m level. Fluorite and coarse-grained calcite are abundant. Anhydrite and dolomite occur as late-stage minerals in vugs (Fig. 7).

PARAGENESIS OF THE CHIMNEY ORES

FIG. 7. Paragenesis of chimney.

Although sphalerite is plentiful, there is not much pyrrhotite in this ore, so that temperature determinations based on the iron content of the sphalerite are somewhat uncertain. Table 2 gives some typical analyses of sphalerite from silicate-bearing chimneys, with minimum temperatures of formation, as given by Kullerud. As noted, these figures are possibly too high.

Massive Sulfide Chimneys

Two principal groups of massive sulfide chimneys are exposed in the mine workings—one along the northeast Torino fault, and the other along a cluster of northwest fractures southwest of the Estrella shaft (Fig. 2). Both of these groups consist of an aggregate of several small chimneys, and both are characterized by massive sulfide ore containing less than 5 percent silicates. The only non-sulfide minerals present are coarsely crystalline, fluorescent calcite, fluorite, and a little anhydrite, which together account for less than 15 percent of the total volume of most ore of this type.

The principal chimney in the group southwest of the Estrella shaft dies out a short distance above the 129-m level, after giving rise to a gently plunging pipe of ore a few meters across, whose emplacement seems to have been controlled by the bedding of the enclosing marble. This is the only known occurrence at Naica of a "manto" similar in origin and form to the "mantos" of Santa Eulalia and other Mexican mining districts.

The mineralogy and paragenetic sequence of the ore in the massive sulfide chimneys is similar to the sulfide mineralogy of the silicate-bearing chimneys,

with only minor variations. The most important difference between the two types of ore is the relative abundance of different minerals. The silicate ore contains less iron (as pyrite and pyrrhotite) than the massive sulfide ore, has a slightly higher ratio of Ag/Pb (Table 1), and a slightly lower ratio of Pb/Zn (Fig. 6). The composition ranges of the two types of ore overlap to a considerable degree, partly because the early silicate ore has been overrun and partly replaced by nearly massive sulfides during the late stages of ore emplacement. The arbitrary 5 percent silicate dividing line between the two types of ore is useful in mapping, but does not take into account the possibility of ore typical of one particular stage in the sequence of deposition impressing its characteristics on ore deposited during an earlier stage.

The pyrrhotite content of the ore in the Torino-Tehuacan chimney increases markedly below the 240-meter level, and pyrrhotite is a major constituent of ore cut by diamond drilling on the 290-m level. In most cores, nearly massive pyrrhotite occurs with remnants of replaced silicates, bordering areas with no silicates in which pyrite is the major sulfide mineral. This behavior suggests that pyrrhotite represents an early stage in the formation of the massive sulfide chimneys, and has been overrun by pyrite during the late stages of ore deposition. The pyrrhotite seems to have been deposited in equilibrium with pyrite, which it envelops, but does not replace.

Kullerud and Yoder (25, 26) have shown that the iron content of pyrrhotite in equilibrium with pyrite varies as a function of temperature and pressure. The pressure effect is relatively minor, so that by assuming a reasonable pressure of formation, an approximate temperature can be determined. The method provides a possible check on the accuracy of the sphalerite "thermometer," and with this in mind, both sphalerite and pyrrhotite from a single sample were analyzed. The sample used came from a diamond drill core that cut the Torino-Tehuacan chimney at about the 335-m level, and contained pyrite, pyrrhotite, sphalerite, and a small amount of chalcopyrite, all of which were apparently deposited in equilibrium with one another. The iron content of the pyrrhotite was measured using the d spacing of the (102) reflection on an X-ray powder photograph (26), and the temperature of formation for an assumed pressure of formation of 500 atm was calculated to be 500° C ± 25°. The associated sphalerite was purified and analyzed chemically for iron, and spectrographically for copper and other impurities. The copper content was less than 0.1 percent, so that the correction for iron present in the chalcopyrite was not large enough to seriously affect the analysis. The sphalerite contained 16.3 weight % FeS, corresponding to a temperature of formation (at 500 atm) of about 565° C ± 10°. As mentioned previously, the temperature of formation as determined by the iron content of sphalerite is theoretically a minimum value. At a constant pressure, an increase in temperature produces a decrease in the metal/sulfur ratio of pyrrhotite (25). If the amount of sulfur available at the time of formation were too low, pyrite would not form at all, and the calculated temperature of formation would be too low. Therefore, the temperature of formation as determined by the pyrrhotite-pyrite "thermometer" should be

a maximum value. The discrepancy between the two methods, and the difficulty in reconciling the sphalerite "thermometer" with the high-low quartz inversion suggests that at these temperatures (500° – 550° C), the sphalerite "thermometer" gives results that are about 50° C too high.

Kullerud et al. (26) found that synthetic pyrrhotite grown at temperatures above 670° C developed a lamellar structure thought to be an exsolution phenomenon of some sort. A similar structure has been found in some natural pyrrhotite, suggesting that the lamellae may be able to survive slow cooling. None of the examined samples of Naica pyrrhotite show these lamellae, suggesting that the temperature of formation of the deposit may not have been greater than 670° C. This figure should be regarded as tentative, pending further work on the significance of these lamellae.

Since pyrite crystallized throughout much or all of the period of ore formation (in both mantos and chimneys), the maximum temperature at any stage of the mineralization in which sulfides were being deposited must have been less than 743° C.

Genesis of the Chimneys

As in the mantos, the sulfides in the silicate-bearing chimneys appear to have been introduced at the same time as the silicates. The evidence is not as compelling as in the mantos, and some of the sulfide in the silicate portions of the Torino-Tehuacan chimney below the 190-m level has almost without question been introduced by a sulfide-rich fluid after the formation of the earlier sulfide-silicate ore.

The first stage in the formation of the chimneys was the introduction into the Tehuacan fracture system of a mineralizing fluid carrying silica, aluminum, magnesium, iron, lead, zinc, copper, manganese, sulfur, arsenic, and fluorine, as well as traces of silver, bismuth, gold, and cadmium. The channelways followed by this fluid diverged upward, resulting in small chimneys and veins of silicate-sulfide ore that converge in depth to form a pipe of silicate ore below the 190-m level. The fluid deposited material in accordance with the observed paragenetic sequence—silicates in general before sulfides (Fig. 7). Possibly some of the pyrrhotite found with silicates below the 240-m level was deposited during the late phases of this stage, which seems to have been gradational in time with the massive sulfide stage.

Apparently the composition of the mineralizing fluid changed with time, so that each of the orebodies represents a sample of the fluid taken at some particular stage in its development. The content of silica and aluminum decreased, and iron in the fluid precipitated as pyrite and/or pyrrhotite. During the last stages of the formation of the massive sulfide ore, the chemical potential of sulfur increased to the point where pyrite formed instead of pyrrhotite. Below the 190-m level, this late-stage fluid, essentially devoid of silica, and carrying large amounts of iron and sulfur, apparently followed more or less the same path as the early silica-bearing fluid. Above the 190-m level, however, this silica-poor fluid followed the Torino fracture system, and deposited massive sulfide ore along this zone on the 190-, 150-, and 120-m

levels. The Torino fracture system must, therefore, have developed during the course of chimney formation. Presumably the massive sulfide chimneys along northwest fractures southwest of the Estrella shaft are contemporaneous with the chimneys along the Torino.

The sulfides deposited during the last stages of chimney formation appear to have crystallized somewhere in the temperature range of 450°–550° C. As with the mantos, it is difficult to estimate the pressure under which the deposit formed. In the silicate chimneys, quartz and calcite occur together in the presence of contemporaneous sphalerite that crystallized at about 500°–550° C (Table 2), suggesting that the partial pressure of CO_2 necessary to prevent the formation of wollastonite was on the order of 100 atm. The figure of 500 atm total pressure used in the evaluation of the pyrite-pyrrhotite and sphalerite "thermometers" is no more than a reasonable guess. (It should be pointed out that an error in the total pressure of 100 percent could be tolerated without seriously affecting the conclusions regarding these two "thermometers.")

GENESIS OF THE PRIMARY ORES OF THE NAICA DISTRICT

The primary ores of the Naica district have been shown to range from pyrometasomatic deposits to bodies of massive sulfides with textures and mineralogy typical of mesothermal ores. A small amount of epithermal ore containing cinnabar has been mined from shallow workings above the central mineralized area. The cinnabar is considered by Bassett (4) to be primary, and was presumably deposited during late-stage hydrothermal (or pneumatolytic) activity at temperatures below about 200° C.

According to the Lindgren depth-temperature system of classification (31), these deposits should show a considerable range in the temperatures and/or pressures at which the various types of ore were deposited. At Naica, however, the ore minerals (sphalerite in particular) in both the "mesothermal" massive sulfide chimneys and the "pyrometasomatic" mantos appear to have formed at about the same temperature. Sphalerite in equilibrium with pyrrhotite from both types of ore contains 17–18 wt% FeS, indicating similar temperatures of formation. The presence of pyrite in both types of ore and of anisotropic grossularite in the mantos indicates a temperature of formation below 743° C, and the exsolved blebs of chalcopyrite in sphalerite from both types of ore indicate a minimum temperature of formation above 350–400° C (6, 9).

The pressure under which the Naica deposits formed is not accurately known. The partial pressure of CO_2 in the last stages of manto formation and during the formation of the silicate chimneys was on the order of 100 atm. Although the late stages of the manto probably formed under conditions of rising CO_2 pressure, as well as falling temperature, it is likely that the total pressure acting on the system during the initial stages of each successive orebody did not change significantly during the period of mineralization as a whole.

Available evidence strongly suggests that the difference between the "pyrometasomatic" and "mesothermal" ores at Naica is due to changes in the composition of the mineralizing fluid with time, rather than to changes in the physical environment of deposition. It has been shown that the fluid responsible for the formation of the mantos introduced both the silicates and sulfides at the same time, and that the sulfides were not introduced by a separate, sulfide-rich fluid during the last stages of manto formation. The mantos were succeeded by silicate-bearing chimneys of sulfide ore evidently deposited by a mineralizing fluid with a considerably lower silicate/sulfide ratio. The silicate-bearing chimneys were in turn succeeded by chimneys of massive sulfide ore that appear to have been deposited by a mineralizing fluid almost devoid of silica, aluminum, and magnesium.

As may be seen from Figure 6, the ratios of lead, iron, and zinc in the sulfides change progressively from manto ore, through sulfide-silicate chimney ore, to the ore characteristic of the massive sulfide chimneys. The change is interpreted as indicating a progressive change in the composition of the mineralizing fluid with time, with late-stage ores containing more iron, and a higher ratio of zinc to lead than ore deposited during the early stages of mineralization in the district as a whole. Similarly, the ratio of Ag/Pb in the fluid appears to have decreased with time (Table 1). The increase in iron is reflected in the silicate mineralogy as well as in the sulfides. The grossularite, vesuvianite, and wollastonite in the early central zone of the manto are succeeded by andradite, tremolite-actinolite, and hedenbergite in the silicate chimney ore. A similar increase in iron with time is shown in the pyrometasomatic ores of the Yerington district (20, p. 36), where brecciated grossularite garnetite has been cemented by andradite. Other minor elements show similar changes from one type of ore to another. Tungsten, for example, is essentially confined to the early manto ore, while arsenopyrite is present in all ore save that of the massive sulfide chimneys.

McKinstry and Kennedy (33) have shown that in many naturally occurring mineral assemblages, the sequence of minerals is such as to suggest that the relative chemical potential of the more volatile component in the assemblage (sulfur, arsenic, etc.) increased in the ore-forming fluid with time. This generalization is borne out at Naica, where an early pyrrhotite-pyrite assemblage is succeeded by massive pyrite. The relative positions of magnetite and specularite in the paragenetic sequence at Naica are also in accord with McKinstry and Kennedy's proposed phase diagram for the system Fe-O-S. According to this diagram, hematite and pyrrhotite are incompatible, and if hematite is to form at all, it should form with pyrite and/or magnetite. In the presence of pyrrhotite, magnetite should be the stable iron oxide. Magnetite and pyrrhotite do occur together in silicate-bearing chimney ore, and were succeeded in time by highly pyritic, massive sulfide ore containing a small amount of specularite.

For this particular system, it is possible to calculate the partial pressures of sulfur vapor and oxygen in the mineralizing fluid at various times during the course of ore emplacement, assuming a constant temperature of formation

of 500° C. The mechanical details of such calculations have been discussed by Krauskopf (22), who presented the results of analogous calculations for a temperature of 600° C. The necessary data for the calculations were taken from Kubachewski and Evans (23), Kelley (18), Latimer (29), and King (19).

During the early stages of the formation of the silicate chimneys, magnetite, pyrrhotite, and pyrite all appear to have been more or less in equilibrium with one another, and all replace ferrous silicates (pyroxene). The reactions of interest in this mineral assemblage are:

$$3Fe_2SiO_4 + O_2 = 2Fe_3O_4 + 3SiO_2$$

$$\Delta F_{500} = -80.7 \text{ kcal}; \quad K = 1/(O_2) = 10^{22.8} \qquad \text{(Eq. 1)}$$

$$3FeS + 2O_2 = Fe_3O_4 + 3/2\, S_2\ (g)$$

$$\Delta F_{500} = -120.2 \text{ kcal}; \quad K = (S_2)^{3/2}/(O_2)^2 = 10^{24.0} \qquad \text{(Eq. 2)}$$

$$2FeS_2 = 2FeS + S_2\ (g)$$

$$\Delta F_{500} = 17.2 \text{ kcal}; \quad K = (S_2) = 10^{-4.9} \qquad \text{(Eq. 3)}$$

From Equation 1, the partial pressure of oxygen in a system in which magnetite is in equilibrium with fayalite is $10^{-22.8}$ atm. As Krauskopf (22, p. 792) has pointed out, this figure is probably too low, since pyroxene rather than olivine is the stable ferrous silicate in deposits of this type. From Latimer's data for the hypothetical compound $FeSiO_3$, and assuming constant enthalpy and entropy changes, it is possible to calculate a rough figure of 10^{-20} atm for the equilibrium pressure of O_2. If magnetite were in true equilibrium with pyrrhotite and pyrite, combining Equations 2 and 3 would give an equilibrium pressure of 10^{-14} atm of O_2. Since the magnetite in these deposits is actually somewhat older than the associated iron sulfides, this figure is probably too large, and a value somewhere between 10^{-20} and 10^{-14} atm seems reasonable.

According to Equation 3, the sulfur vapor pressure during the pyrrhotite-pyrite phase of chimney development was about 10^{-5} atm. During the latter stages of ore formation, the reaction symbolized by Equation 3 was displaced to the left, and pyrite was deposited rather than a pyrrhotite-pyrite assemblage. This shift could have been brought about by either of two mechanisms (33), both of which were probably operative in this particular deposit. The first and most obvious is the possibility that the vapor pressure of sulfur in the mineralizing fluid increased with time, and that the temperature remained the same throughout the entire course of ore deposition. It is probable that the temperature did fall during the last stages of the crystallization of any individual orebody. In this event, the pyrite-pyrrhotite reaction (Eq. 3) would be shifted to the left even if the vapor pressure of sulfur in the mineralizing fluid remained the same. At 500° C, the equilibrium pressure of sulfur vapor is $10^{-4.9}$ atm. At 400° C, the equilibrium pressure is $10^{-8.5}$ atm. If, therefore, a fluid containing $10^{-4.9}$ atm of sulfur vapor at a temperature of

500° C were depositing pyrrhotite and pyrite together, the same fluid at 400° would deposit pyrite to the exclusion of pyrrhotite, and would, in fact, replace early-formed pyrrhotite with pyrite.

In addition to the change in the chemical potential of sulfur, the oxidation state of the mineralizing fluid appears to have changed during the cooling of each successive orebody. The oxidation state of the initial fluid introduced into each of the orebodies need not, and probably did not change drastically with time. Consider the reaction:

$$CaSiO_3 + SO_2 + \tfrac{1}{2}O_2 = CaSO_4 + SiO_2$$
$$\Delta F_{500} = -66.06 \text{ kcal}; \quad K_{500} = 10^{18.6}$$
$$\Delta F_{400} = -69.87 \text{ kcal}; \quad K_{400} = 10^{22.6} \qquad \text{(Eq. 4)}$$
$$K = 1/(SO_2)(O_2)^{\frac{1}{2}}$$

It has been shown that during the early stages of both manto and chimney orebodies the partial pressure of oxygen in the mineralizing fluid was probably somewhere between 10^{-14} and 10^{-20} atm. (It should be re-emphasized that the early stages of both these orebodies apparently formed at about the same temperature—a figure of 500° C is taken for purposes of illustration.) For an oxygen pressure of 10^{-20} atm, the equilibrium partial pressure of SO_2 is $10^{-8.6}$ atm. The corresponding pressure of SO_2 at 400° C is $10^{-12.6}$ atm. Therefore, if the mineralizing fluid at 500° C contained 10^{-20} atm of O_2 and say 10^{-10} atm of SO_2, wollastonite (or a pyroxene) would form rather than anyhydrite. At 400°, however, the *same* fluid would deposit anhydrite and quartz rather than a silicate. This mechanism provides a ready explanation for the occurrences of low-quartz and anhydrite lining vugs in pyroxene (hedenbergite).

The anhydrite in each of the various types of ore at Naica was invariably deposited toward the end of the period of crystallization of the particular orebody in which it is found, at a time when large-scale movement of mineralizing fluids through the orebody had apparently ceased. If the anhydrite in each of the three main types of ore (manto, silicate chimney, and massive sulfide chimney) was deposited due to an increase in the partial pressure of SO_2 in the mineralizing fluid, it would be necessary to postulate that the SO_2 pressure rose and fell at least three times during the course of ore deposition in the district as a whole. This seems somewhat unlikely, especially in view of the relatively constant shift in the overall composition of the ore-forming fluid with time, and it seems far more reasonable to suggest that the anhydrite at Naica was deposited from residual fluids, as a consequence of falling temperatures during the last stages of the crystallization of each separate orebody.

It is interesting to note that the inferred gross changes in the composition of the ore-forming fluid with time are virtually identical with the changes in composition due to progressive reaction with limestone. It has been shown that the hedenbergite-quartz-calcite zones of the Azules-Navacoyan manto are depleted in aluminum, tungsten, and silver, and enriched in iron, relative to the central wollastonite-grossularite-vesuvianite zone (Fig. 6). It seems

possible that if this "reaction differentiation" had gone on long enough, most, or all, of the silica, aluminum, and magnesium in the fluid would have been removed in the formation of silicates, leaving a fluid capable of depositing essentially pure sulfides. The mechanism provides a highly probable explanation for the small veins of sulfides associated with the mantos. One of the principal difficulties in applying the suggestion to the sequence of mineralization in the district as a whole is the problem of accounting for the distribution of copper in the various orebodies. The existence of the "copper mantos" suggests that copper was enriched during the course of "reaction differentiation" in the normal silicate mantos. Although some of the chimney ore contains a percent or so of copper, the amount of copper present is not comparable with the amount that would be expected if the chimneys were strictly the end products of a process of selective deposition such as has gone on in the mantos. It is possible, of course, that the "copper mantos" were not deposited by fluids that leaked away from the main mantos, even though their distribution suggests this mechanism of formation. Finally, it is possible to appeal to a decrease with time in the copper content of the fluid emanating from the inferred intrusive body "at depth". Just as this suggestion is free of contradictory evidence, so is it insusceptible of proof.

If the progressive change in the composition of the fluid responsible for the deposition of the Naica ores was due to selective precipitation, it must follow that iron was more soluble than either lead or zinc, and that zinc was slightly more soluble than lead under these particular conditions. The relative positions of iron and zinc as compared with lead are similar to the sequence of total vapor pressures of these elements (as chlorides) that would be expected in a vapor at 600° C in equilibrium with solid sulfides, but the relative positions of iron and zinc are reversed (22, p. 802). It seems possible, however, that the figures given by Krauskopf could be reversed (as well as increased) by factors such as the simple solubility of sphalerite and iron sulfides in a compressed vapor or supercritical fluid.

OXIDATION

The primary sulfide ores at Naica have been oxidized down to about the 130-m level. In some of the dense silicate ore of the mantos, relict sulfides are present on the 18-m level, and in some of the chimney ore, ground water circulating along fractures has resulted in the formation of oxides down at least to the 190-m level.

The principal minerals developed during the oxidation of the primary ores are hydrous iron oxides of various types, manganese oxides, anglesite, cerrusite, and gypsum. The silicates have largely been destroyed in former high-grade ore, and a little chalcedony, some chrysocolla, and a trace of hemimorphite are present in oxidized silicate ore. Small amounts of malachite, azurite, cuprite, brochantite, conichalcite, smithsonite, and native copper are present in the oxide zone, and native silver, wufenite, cerargyrite, and various sulfantimonides of silver have been reported.

One of the most striking features of the oxidation at Naica is the almost complete removal of zinc from ore that must once have contained roughly equal amounts of galena and sphalerite. A rough estimate, based on past production figures, suggests that on the order of 50,000 tons of metallic zinc have been removed from the various orebodies during oxidation. The small amounts of smithsonite and hemimorphite found in the mine cannot begin to account for this zinc, which seems to have been flushed out of the system altogether. Deep circulation of ground water seems to have been controlled by a few large fractures or fracture zones, and it appears that these fractures served as conduits that carried weakly acid, zinc-bearing solutions well beyond the areas now exposed by mining or explored by diamond drilling.

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Nov. 30, 1958

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Economic Geology
Vol. 54, 1959, pp. 1035–1039

THE SOLUBILITY OF ZINC SULFIDE IN WATER AT HIGH TEMPERATURES

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ABSTRACT

From experiments, the solubility of zinc sulfide in water is less than 5×10^{-6} mole per kilogram in the temperature range 200–300° C. This is in agreement with calculations from thermodynamic data.

The transport of metal sulfides in hydrothermal solutions is briefly discussed and thiosulfate complexes of heavy metals are suggested to be important agents in this respect.

INTRODUCTION

THE mechanism of formation of natural metal sulfide deposits remains a problem to both geologists and geochemists.

Thermodynamic calculations of the solubilities of metal sulfides in water at high temperatures by Verhoogen (16), and by Garrels (3) suggest that the solubilities of heavy metal sulfides remain very small, but that the solubilities of zinc and iron sulfides increase to appreciable values (Table 1).

TABLE 1

SOLUBILITIES AT 300° (MOLES/LITER)

ZnS	1.2×10^{-2}	PbS	3×10^{-5}
FeS	2×10^{-4}	Ag_2S	3×10^{-13}
CoS	1×10^{-4}	CuS	8×10^{-14}
FeS_2	8×10^{-5}	HgS	1×10^{-17}

Calculated for pH 7 by Verhoogen (16).

If the values in Table 1 were correct the solubility of zinc sulfide would be in a range convenient to measure in liquid water up to the critical temperature by means of the single crystal technique.

EXPERIMENTAL RESULTS

The solubility of single natural sphalerite crystals from Joplin, Missouri, was determined in water up to 300°. The crystals used were clear and light brown in color.

A bomb with a test-tube shaped Teflon liner was used. A tight-fitting Teflon plug was pushed into the bore of the liner down to the level of the liquid so there was no vapor phase above the solution containing the crystal. 20 cc of water were placed in the liner with the weighed crystal, and nitrogen,

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freed from oxygen by passing it over hot copper, was bubbled through for approximately an hour. The Teflon plug was then quickly pushed in. About 1 cc of water was added in the free space above the plug, to equalize steam pressures at high temperatures, and nitrogen was also bubbled through this liquid. With the bomb full of nitrogen the head was screwed on, and the bomb finally evacuated to the pressure of saturated water vapor at room temperature. After the run the crystal was again weighed on a microbalance.

By using the procedure above it was hoped to minimize the oxygen left in the bomb and prevent solution of zinc sulfide simply by oxidation.

The results obtained are given in Table 2. The amounts dissolved do not increase or decrease with temperature in any systematic manner, and therefore cannot be taken as representing true solubilities.

The amounts dissolved (approximately 20 micrograms) possibly represent the oxygen remaining in the bomb in each experiment. If oxidation of zinc sulfide to zinc oxide, followed by solution of the latter is considered, 20 micrograms of sulfide would combine with about 3 micrograms of oxygen. It would be very difficult to prove that this small quantity of oxygen was not left in the bomb.

The true solubility of zinc sulfide at 300° is evidently less than about 5×10^{-6} m (moles per 1,000 g water). Morey and Hesselgesser (9) found that the solubility of sphalerite in water at 500° and 1,000 bars pressure was less than 0.001 percent, or 10^{-4} m.

In his calculations Verhoogen assumed that the first and second acid dissociation constants for hydrogen sulfide (K_1 and K_2) increased steadily with temperature. It is now generally recognized (4) that with increasing temperature the dissociation constants of weak acids in liquid water increase, pass through a maximum, and decrease again.

TABLE 2

T°C	Time (hours)	Amount Dissolved (moles/kilogram) $\times 10^5$
194	30	0.6
197	20	0.7
199	50	1.3
224	24	3
225	70	0.7
225	70	0.8
229	24	0.7
232	24	0.9
232	24	1.1
237	150	0.7
250	70	0.0
263	70	0.0
265	24	2.0
266	24	2.0
268	50	0.5
273	70	1.5
275	24	0.0
279	50	1.5
300	30	1.2

TABLE 3

T°C.....	25	100	150	200	250	300
$K_1 \times 10^7$	0.95	2.05	1.95	1.45	0.92	0.54
$K_2 \times 10^{14}$	1.4	70	300	700	1,200	1,500
$K_w \times 10^{14}$	1.0	52	240	490	520	400

(Molal Scale.)

The values of K_1 and K_2 were recalculated for temperatures up to 300° using the general formula of Pitzer (13).

$$\log K = A/T + 53.78 - 20 \log T.$$

The values of K_1 and K_2 at 25° are those of Ellis and Golding (2). Table 3 also includes interpolated values for the ionic dissociation of water K_w from the results of Noyes (11).

The solubility product of zinc sulfide (sphalerite) was calculated from the following information. For the reaction

$$\text{ZnS (sphalerite)} \rightarrow \text{Zn}^{++} \text{ (soln.)} + \text{S}'' \text{ (soln.)}$$

Latimer (7) gives the standard change in Gibbs free energy, $\Delta G°$, as 34,320 cals mole^{-1} and the standard change in heat content, $\Delta H°$, as 20,630 cals mole^{-1}. For processes of this type in which two ions are formed from a solid or a molecule the change in heat capacity of the system $\Delta C_p°$ is often of the order of -30 to -60 cals deg^{-1} mole^{-1}. $\Delta C_p° = -45$ to -60 for the second ionization step of weak acids (Harned and Owen, 4); $\Delta C_p° = -35$ to -41 for the solution of AgCl, AgBr and AgI in water (Owen and Brinkley, 12). A value of $\Delta C_p° = -50$ was assumed for the solution of zinc sulfide. Table 4 gives the values obtained for the free energy of solution $\Delta G°$ at higher temperatures and also values for the solubility product (P).

$$\Delta G° = -RT \ln P.$$

From knowledge of the values of P, K_1, K_2 and K_w the solubility (S) of sphalerite was obtained at various temperatures both for pure water (as used in the experiments) and for a solution of pH 7. The values of S are in moles/1,000 g water.

TABLE 4

T°C.....	25	100	200	250	300
$\Delta G°$	34,320	38,210	44,550	48,160	51,930
P	6×10^{-26}	3×10^{-23}	2×10^{-21}	6×10^{-21}	1.3×10^{-20}
S (water)	9×10^{-10}	1.2×10^{-8}	1.0×10^{-7}	1.7×10^{-7}	3×10^{-7}
S (pH 7)	9×10^{-10}	2.5×10^{-8}	7×10^{-8}	1.0×10^{-8}	1.6×10^{-8}

The values of S in pure water were obtained by use of the following approximate relationship.

$$S^2 = P\left(1 + \frac{K_w^{\frac{1}{2}}}{K_2} + \frac{K_w}{K_1 \cdot K_2}\right).$$

The maximum solubilities obtained in the experiments show that the true values of P cannot be much greater than those given in Table 4.

The results show that the solubility of zinc sulfide is very slight in liquid water at all temperatures. The solubilities of other metal sulfides in water at high temperatures will also be even less than predicted by Verhoogen.

THE TRANSPORT OF METAL SULFIDES IN HYDROTHERMAL SOLUTIONS

Because of the insoluble nature of the heavy metal sulfides in liquid water even at high temperatures, quite unreasonable quantities of their pure saturated solutions are required to pass through a rock vein in order to produce the quantities of sulfide ore found in a major natural deposit.

It is generally recognized that factors other than the simple metal sulfide-water equilibrium must be considered in the transport of metal sulfides in natural hydrothermal solutions.

As indicated by Garrels (3) there are three main lines of thought on this process amongst geologists. One group considers that sulfides are transported in solutions with sufficient acidity to repress considerably the sulfide ion concentration. Other workers, especially Smith (15) consider that the metal sulfides are held in solution as alkali sulfide complexes. As a third possibility it has been suggested by Lindgren (8) that metal sulfides are carried as colloidal suspensions in the hydrothermal fluid.

It is not considered that the last two proposals are of general validity although each may be important in special cases, e.g., the transport of gold as a colloid (15), and of mercury as the HgS_2'' ion (6).

As sampled hydrothermal solutions invariably have a high carbon dioxide content, it is difficult to see that the hydroxyl ion concentration could be appreciably greater than that for neutral water at any temperature.

Newhouse (10) has shown that the zinc-lead sulfide ores in the Mississippi Valley were probably formed at low temperatures in the range 80–135° C, and that liquid inclusions in the ore contain 12–25% NaCl. With the concentrations of salts usually found in hydrothermal solutions it seems unlikely that colloidal metal sulfide solutions would be stable.

It is possible that low temperature deposits of this type were caused by transport of lead and zinc in acid solutions, and possibly also as complexes of type $PbCl^+$ as suggested by Hemley (5), but another possibility which does not seem to have received any attention is suggested below.

The writer has shown (1) that the composition of magmatic gases changes with temperature in the manner predicted for a thermodynamic equilibrium between the constituents. In high-temperature gases the constituents tend to be H_2–SO_2–CO–CO_2, while in the low temperature gases in equilibrium with hot-spring waters, H_2S and CO_2 predominate.

It is possible for polythionates and thiosulfates to form in waters in contact with H_2S and SO_2, and polythionates have been found in waters from the more active New Zealand thermal areas (17). Thiosulfates are a common breakdown product of polythionates.

A recent paper by Schulek et al. (14) on the products from the hydrolysis of sulfur in water at 100° indicated that hydrogen sulfide, thiosulfates and sulfur dioxide can be formed. The presence of thiosulfate may easily have been overlooked in the analyses of hydrothermal solutions, and its concentration included with that of the more obvious constituent, hydrogen sulfide. As many heavy metals form soluble complex thiosulfates, e.g., $Ag(S_2O_3)^-$, $Ag(S_2O_3)_2^{3-}$, it is suggested that these compounds are much more important in the transport of heavy metals in hydrothermal solutions than has been considered previously.

ACKNOWLEDGMENTS

The author thanks Dr. W. S. Fyfe for the sphalerite crystals used in this work, and Mr. V. J. Chettleburgh for numerous micro-weighings.

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Economic Geology
Vol. 54, 1959, pp. 1040–1046

EFFECT OF FeS ON THE UNIT CELL EDGE OF SPHALERITE. A REVISION[1]

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ABSTRACT

The relationship between the unit cell edge of Fe-bearing sphalerites and their compositions has been redetermined. The equation relating the unit cell edge of sphalerite (a_o) to the FeS content is $a_o = 5.4093 + 0.000456X$, where a_o is in Ångstrom units and X is mole percent FeS in solid solution in the sphalerite. This curve is significantly different from that determined by Kullerud (6) and the difference is believed to be due to the use of partially oxidized FeS in the original runs. If this supposition is correct, a little less iron would substitute for zinc in ZnS than indicated by Kullerud (6). The difference between the solvus curve obtained by using unoxidized FeS and that obtained by using somewhat oxidized FeS may be significant, at least at high temperatures. This difference means that Kullerud's FeS-ZnS solvus must be used with caution when employed in determining high geologic temperatures, in particular those above 600° C.

INTRODUCTION

THE system FeS-ZnS was the subject of an extensive study by Kullerud (6), in which he developed the now widely used sphalerite geothermometer. The solvus curve, relating the amount of FeS that goes into solid solution in ZnS at various temperatures, was determined by Kullerud (6) by means of the unit cell edge versus composition curve given in Figure 1. Recent studies in systems involving ZnS and FeS have shown that Kullerud's original spacing curve is in error. The present work corrects this relationship.

The discrepancy in the results of the present study and those of Kullerud (6) may be explained in the light of recent research on the oxidation of certain sulfides such as FeS and the pyrrhotites ($Fe_{1-x}S$), (Kullerud, in preparation) and on the ability of oxygen to replace sulfur in ZnS (8). The FeS used by Kullerud to determine his original spacing curves seems to have been partially oxidized by contact with the atmosphere. Any oxidation of the FeS will reduce the effective, or available, FeS in the initial charge and provide a source of oxygen to enter the sphalerite structure, causing a consequent reduction in the unit cell volume of the sphalerite (8).

This report is a combination of results obtained in various laboratories. Skinner synthesized the samples labelled S in Table 2. Some of these were prepared and the unit cell edges measured, at the University of Adelaide, South Australia, and the others were prepared in the laboratories of the U. S. Geological Survey, Washington, D. C. Barton synthesized the samples labelled

[1] Publication authorized by the Director, U. S. Geological Survey.

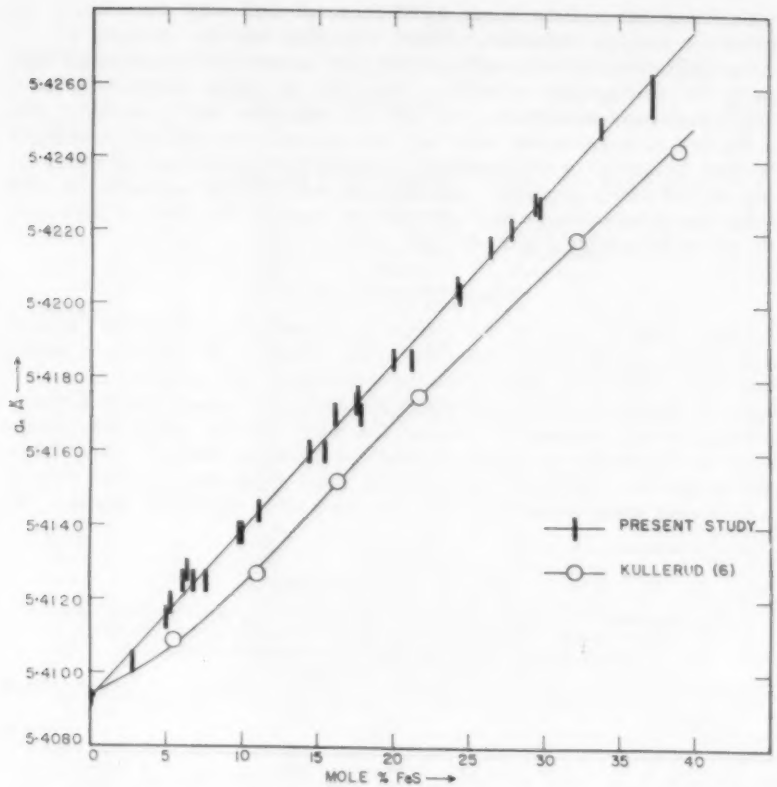

FIG. 1. Comparison of relation between unit cell size and composition of Fe-bearing sphalerites from the present study and from Kullerud (6). Kullerud's measurements have been corrected for conversion of kX to Å units and for errors in mole percent calculations.

B in Table 2. Some were prepared and initial X-ray measurements were made at the Geophysical Laboratory, Carnegie Institution of Washington, under the direction of Kullerud, in a study of the system FeS-ZnS-S (1), and the remainder were prepared and the unit cell edges measured in the laboratories of the U. S. Geological Survey, Washington, D. C., using separate apparatus from that employed by Skinner. All of Barton's unit cell edge measurements have been repeated by Skinner and the two sets of data are in excellent agreement. This diversity of effort and equipment reduces to a minimum any constant or instrumental errors and allows us to place considerable confidence in the final results.

Buck and Strock (3), Smith (9) and others have indicated that mixed

cubic-hexagonal packing forms (polytypes) of ZnS may form below the sphalerite-wurtzite transition. These polytypes can be characterized by X-ray diffraction methods, and since they are anisotropic in transmitted light under the petrographic microscope, they can be readily detected optically. The sphalerites measured for our unit cell edge data were essentially cubic at the time of measurement, since they were optically isotropic and no evidence of either hexagonal or rhombohedral symmetry could be detected on the X-ray powder diffraction patterns. Our data are thus directly applicable to cubic sphalerite and no attempt has been made to evaluate the effect of ZnS polytypism on the solubility of Fe in ZnS.

SAMPLE PREPARATION

The sphalerite used in the present work was prepared at 900° C from high purity zinc metal and elemental sulfur (Table 1) by reaction in sealed, evacuated, silica-glass tubes. The vapor volume in the tube was reduced as much as possible by inserting silica-glass rods having approximately the same diameter as the internal diameter of the tubes. Excess sulfur was always added to ensure that no oxygen entered the sphalerite structure (8). When the charges were cooled, the excess sulfur vapor condensed as visible globules which were easily separated from the clean white sphalerite powder. To

TABLE 1

ANALYSES OF REAGENTS USED

Zinc, spectrographic analysis by American Smelting and Refining Co.; iron (N.B.S. standard sample 55d) average of 8 analyses reported by National Bureau of Standards; sulfur (Freeport Sulphur Co.), spectrographic analysis by K. V. Hazel, U. S. Geological Survey.

Elements	Zinc	Iron	Sulfur
Al	—	0.002%	—
As	—	.009	0.0003%
Ba	—	—	.0003
Bi	—	—	.001
C	—	.0106	<.01
Ca	—	—	.0001
Co	—	.007	—
Cr	—	.005	—
Cu	0.0005%	.056	—
Fe	—	Major	—
Ge	Tr.	—	—
Mg	—	—	.0003
Mn	—	.030	—
Mo	—	.001	—
N	—	.004	—
Ni	—	.010	—
P	—	.005	—
Pb	.0005	—	.0003
S	—	.014	Major
Sb	Tr.	—	—
Si	—	<.001	—
Sn	—	.005	—
V	—	<.001	—
Zn	Major	—	—

TABLE 2

UNIT CELL EDGES OF FE-BEARING SPHALERITES

FeS content		Temperature of synthesis, °C	Unit cell edge, Å	Method of measurement	Sample prepared by[1]
Weight percent	Mole percent				
0	0	600–1,000	5.4093±0.0002	Skinner and Barton (8)	S, B
2.52	2.80	930	5.4103±0.0003	Diffractometer	S
4.53	5.00	850	5.4115±0.0003	Diffractometer and film	B
4.78	5.27	930	5.4119±0.0003	Diffractometer	S
5.51	6.10	920	5.4125±0.0003	Diffractometer and film	B
5.80	6.40	920	5.4128±0.0003	Diffractometer	B
6.19	6.84	870	5.4125±0.0003	Film	S
6.94	7.68	930	5.4125±0.0003	Diffractometer and film	S
8.93	9.83	870	5.4138±0.0003	Film	S
9.11	10.00	850	5.4138±0.0003	Diffractometer	B
10.15	11.12	930	5.4144±0.0003	Diffractometer	S
13.30	14.45	870	5.4160±0.0003	Film	S
14.25	15.50	920	5.4160±0.0003	Diffractometer	B
14.95	16.25	870	5.4170±0.0003	Diffractometer and film	S
16.20	17.60	920	5.4173±0.0003	Diffractometer	B
16.24	17.64	870	5.4175±0.0003	Film	S
16.46	17.88	930	5.4170±0.0003	Diffractometer	S
18.40	20.00	850	5.4185±0.0003	Diffractometer	B
19.59	21.20	930	5.4185±0.0003	Diffractometer and film	S
22.45	24.30	870	5.4205±0.0003	Film	S
22.55	24.40	920	5.4203±0.0003	Diffractometer and film	B
24.45	26.40	920	5.4216±0.0003	Diffractometer	B
25.84	27.85	890	5.4221±0.0003	Diffractometer	S
27.32	29.42	860	5.4228±0.0003	Diffractometer	S
27.65	29.75	890	5.4227±0.0003	Film	S
31.48	33.78	890	5.4249±0.0003	Diffractometer	S
34.78	37.20	890	5.4258±0.0006	Diffractometer	S

[1] S refers to samples prepared by Skinner, B to those prepared by Barton.

ensure that all free sulfur had been removed, the ZnS prepared by Skinner was heated to approximately 600° C for half an hour in a continuously evacuated glass tube. This caused any remaining free sulfur to vaporize and be removed by the vacuum pump. The ZnS prepared by Barton had the sulfur removed by crystallizing it at 100° C for one hour and then washing the charge with carbon disulfide, which dissolved all the free sulfur.

The FeS used as a starting material was prepared by heating iron pellets (N.B.S. Open Hearth Iron, 55d, Table 1), and sulfur in stoichiometric proportions to form FeS, in sealed, evacuated, silica-glass tubes. The iron and sulfur mixture was heated for at least 48 hours at 600° C to give a bright metallic button of FeS. It is not necessary to add additional sulfur to the charges to compensate for the sulfur in the vapor volume in the sealed tubes as the vapor pressure of FeS at 600° C is exceedingly low and hence the amount of sulfur actually in the vapor space is negligibly small. Microscopic examination was necessary to ensure that all the iron had reacted with sulfur. Since FeS is susceptible to oxidation, it was always stored under acetone. Most ZnS-FeS runs were weighed out within a few hours of opening the FeS tube. By these precautions no measurable changes occurred in the FeS starting material.

Mixes of ZnS and FeS from 50 to 1,000 milligrams in weight were carefully ground together and immediately sealed in evacuated silica-glass tubes. The mixtures were heated from 5 to 30 days, at temperatures ranging from 800° C to 950° C, depending upon the composition, so as to heat to as high a temperature as possible, yet still be within the sphalerite stability field. It was observed that mixes having more than 100 milligrams of sulfide, or containing more than 12 percent FeS by weight, required one or more regrindings and reheatings to produce homogeneous phases. The presence or absence of free FeS was readily checked by a hand magnet or microscopically by reflected light. The homogeneous distribution of Fe in the sphalerite structure was easily checked by noting that sharp peaks were present on the X-ray diffraction patterns. Nonhomogeneous mix-crystals gave broad, asymmetric intensity profiles for each diffraction line. Sharp diffraction patterns, giving constant unit cell dimensions after successive heatings, thus provided a sensitive test for homogeneity.

UNIT CELL MEASUREMENT

Measurements of the unit cell edge were made in two ways. The first method was by X-ray powder diffraction photographs taken in 114.59 mm diameter cameras, using Ni filtered CuKα radiation ($\lambda = 1.54050$ Å). Sharp back reflection lines were obtained in which the Kα_1 and Kα_2 reflections were clearly resolved. The (531), (620), (533), and (444) lines were measured, and the measurements corrected for film shrinkage. The values of a_o calculated from each line were plotted against the Nelson and Riley (7) function, and the curve so obtained extrapolated to 180° 2θ, eliminating the need for internal standards.

The second method of measurement was by Norelco X-ray diffractometer, with Ni filtered CuKα radiation. Smear mounts on glass slides were prepared with analytical reagent NaCl as an internal standard. The unit cell edge of NaCl was taken as 5.62891 kX at 20° C (5). This was converted to 5.64028 Å at 20° C by the conversion factor 1.00202 Å/kX [2] (2). The sphalerite (422) and (331) lines were measured relative to the NaCl (422) and (420) lines. A number of samples were also checked against pure CaF_2, by comparing the (620) line of sphalerite against the (620) line of CaF_2. The values obtained were not included in Table 2 but were in close agreement with those obtained by reference to NaCl, and with those obtained from film measurements.

Individual lines on the diffractometer charts were measured by projecting the averaged center-lines of the intensity profiles to background radiation level and measuring the intersection point with the background to $\pm 0.01°$ 2θ. This ensured that any instrumental, or constant errors, were handled in the same way in each measurement, and hence that measurements of different runs are directly comparable.

[2] The precision indicated for both the unit cell edge of NaCl and the kX to Å conversion factor are much higher than the accuracy of our measurements on the diffractometer. Thus, even if the precisions of NaCl unit cell edge and the conversion factor are misstated by a factor or two or three, we are justified in using them for our comparative measurements.

RESULTS

The unit cell edges obtained from the described runs are presented in Table 2. Three charts or films were measured for each sample, and the uncertainty of measurement is ± 0.0003 Å in both cases. Stoichiometric sphalerite was the subject of a detailed study by Skinner and Barton (8), who found that it has a unit cell edge of 5.4093 ± 0.0002 Å. The straight line shown in Figure 1 is the least squares fit to the data in Table 2 and has the equation

$$a_0 = 5.4093 + 0.000456X,$$

where a_0 is the unit cell edge of a sphalerite containing X mole percent FeS. The uncertainty in a_0 is ± 0.0003 Å.

Coleman (4) presented a unit cell edge versus composition curve for Fe-bearing sphalerites. Unfortunately he did not present his data numerically, but as closely as we can determine from his curve, our results are in excellent agreement with his.

CORRECTION OF EARLIER MEASUREMENTS

Kullerud's (6) measurements of the effect of FeS on the unit cell edge of sphalerite require a correction factor before they can be compared with the present measurements. This correction arises from the unit cell edge Kullerud selected for the NaCl used as an internal standard. The figure selected was actually in kX units but was incorrectly quoted in Å units. To correct these measurements, the kX to Å conversion faction (2) should be applied. There is also a minor error in Kullerud's conversion of mix-crystal composition from weight percent to mole percent. The corrected values of the measurements and compositions are presented in Table 3, and graphically in Figure 1. The agreement between Kullerud's corrected measurements and the present work is excellent for pure sphalerite, but the two curves rapidly diverge with increasing FeS content. The good agreement for pure ZnS and consistent measurements of the original materials indicate that the divergence is not due to measurement errors, but rather to partial oxidation of the FeS sample

TABLE 3

UNIT CELL SIZES OF FeS-BEARING SPHALERITES DETERMINED BY KULLERUD (6)

Corrected for conversion of kX to Å units and for errors in mole percent calculations

FeS content		Unit cell size, Å	
Weight percent	Mole percent (corrected)	Original	Corrected
0	0	5.3985 ±0.0001	5.4094 ±0.0001
5.0	5.5	5.4000 ±0.0002	5.4109 ±0.0002
10.0	11.0	5.4018 ±0.0002	5.4127 ±0.0002
15.0	16.3	5.4043 ±0.0002	5.4152 ±0.0002
20.0	21.7	5.4066 ±0.0002	5.4175 ±0.0002
30.0	32.2	5.4109 ±0.0002	5.4218 ±0.0002
36.5	39.0	5.4134 ±0.0002	5.4243 ±0.0002

Kullerud used in preparing his charges. Any oxidation of the FeS sample would reduce the FeS available to enter the ZnS structure. This would cause the spacing curve determined with oxidized FeS to diverge continually from that determined with unoxidized FeS at higher concentrations of FeS. The oxidation of FeS (Kullerud, in preparation) when exposed to air proceeds rapidly and measurable changes can be observed after one day. Consequently it is required that all FeS be stored under an inert liquid such as acetone or toluene.

Since both water vapor and oxygen have significant solubilities in acetone, adequate precautions must be taken to ensure that the original acetone covering the FeS is free of both water and oxygen. Later work has indicated that benzene and toluene are preferable to acetone as covering liquids for materials subject to oxidation.

DISCUSSION

A consequence of this revision of the unit cell edge-composition relation is that the earlier determination of the FeS-ZnS solvus may have to be revised. Using the corrected cell edges measured by Kullerud (6) for sphalerites in equilibrium with FeS at different temperatures, our spacing curve indicates that Kullerud's solvus should be raised. However, the probable presence of oxygen in Kullerud's original runs may have affected the solubility of FeS in ZnS. The magnitude of this effect has not yet been evaluated, but this work is under way by Kullerud at the Geophysical Laboratory at present. Temperature determinations using the sphalerite geothermometer based on the original solvus curve should be viewed with caution pending further studies.

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Washington, D. C.,
January 22, 1959

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Economic Geology
Vol. 54, 1959, pp. 1047–1055

QUANTITATIVE MINERALOGY IN 30 MINUTES[1]

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ABSTRACT

A common basis of petrographic descriptions of acid igneous rocks rests upon the quantitative determination of quartz content and feldspar types and contents. With these fundamental determinations almost all of these igneous rocks may be placed in their correct categories. In general, the quantitative determination of the ferromagnesian and other accessory minerals is not essential to the classification of these rocks. Much of this basic information necessary for rock classification is now obtained at the Kennecott Research Center by use of the infrared spectrophotometer. From standard calibration curves obtained by using individual pure minerals, and with the aid of synthetic mixtures of the diagnostic minerals, the quantities and types of minerals present in the unknown samples can be rapidly determined. To test the validity of the analytical results obtainable by this method, the standard granite (G-1) was used, which had been originally prepared and distributed as a powder by the U. S. Geological Survey for spectrographic and chemical analyses. This, therefore, constituted a good rock sample whose mineralogical composition was known, and was particularly useful as most igneous rocks associated with orebodies are of this acidic type—granites, granodiorites, monzonites and quartz monzonites.

INTRODUCTION

THE use of the infrared absorption spectrophotometer for structural studies and analysis in organic chemistry has been well known for a long time. Recently it has found added usage in the inorganic and mineralogical fields although its value as a quantitative tool in mineralogy has been little utilized (4–11). In the past three years over 4,000 infrared curves of mineral samples, rocks and other inorganic materials have been prepared by the Kennecott Research Center. During this period, the instrument has been of increasing value for quantitative as well as qualitative mineralogy, and provided a rapid and particularly reproducible method for the examination of samples, rocks and mineral specimens submitted by the Exploration Department of the Corporation.

The method has several distinct advantages. The sample can be taken directly in powdered form from an assay pulp (at minus 200 mesh) as submitted to the assay department for wet chemical analysis; thus, the petrographic data deduced from the infrared analyses are obtained on the same sample undergoing chemical analysis. The same care that goes into all stages of collection and preparation of assay samples is available therefore

[1] This paper was presented at the Rocky Mountain Minerals Conference, sponsored by the Utah Section AIME, Salt Lake City, Utah, September 17, 18 and 19, 1958.

for the preparation of the sample for infrared analysis. The effect of grain size on the infrared absorption curve of a rock or mineral is minimized by grinding a 10 mg sample under alcohol to minus 5 microns (50% minus 2 microns). The method thus finds itself admirably suited to the petrography of fine grained or even cryptocrystalline rocks; in fact, excellent spectra can be obtained with samples that would be judged amorphous by x-ray diffraction. Importantly, the petrography of a sample can be determined even if that sample is a small grain, a rock chip or the bulk integration of many hundreds of feet of drill core.

EXPERIMENTAL PROCEDURE

Infrared absorption spectra were obtained with KBr discs containing ¼ percent of the sample in question. These discs were prepared by adding 2.50 mg of a preground sample to 1.00 gm of KBr (Harshaw Infrared quality), blending with a "Wig L Bug" amalgamator, weighing out enough of the blend to form a 12 mm diameter disc of the desired thickness, and pressing under 12.5 tons pressure in a vacuum die. The absorption curves were obtained using a Perkin Elmer Model 21 spectrophotometer with rock salt optics.

RESULTS

The absorption curve obtained from the standard granite sample G-1 prepared by the U. S. Geological Survey (3) is shown in Figure 1. On this curve have been recorded the percentages of the constituent minerals as determined using simultaneous equations based upon the curves of the con-

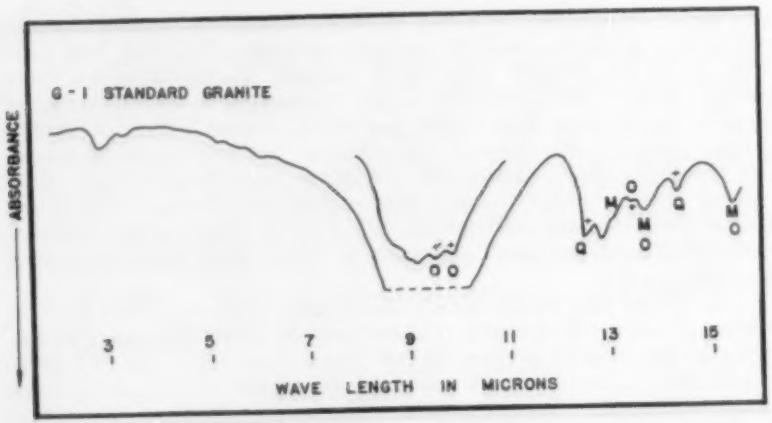

FIG. 1. Infrared absorption spectrum of the standard granite G-1, showing data for mineral composition and the portions of the curve from which they are read. +, diagnostic peaks; Q, quartz (36%); M, microline (29%); O, oligoclase (23%).

TABLE 1

MINERALOGICAL COMPOSITION OF STANDARD GRANITE (G-1)

Mineral	Average as published[1] (Chayes—Ref. 3)	KRC infrared determination[2] (3 separate runs)		
		A	B	C
Quartz	27.7%	37%	36%	35%
Potash feldspar—Microcline[3]	34.1	30	28	28
Plagioclase—Oligoclase An_{20} [4]	31.3	22	22	25
Biotite	3.5	ND	ND	ND
Muscovite	1.4	ND	ND	ND
Opaque accessories	1.5	ND	ND	ND
Non opaque accessories	0.5	ND	ND	ND
	100.0	89	86	88
		(Balance IR-inert)		

[1] Recalculated to weight percent.
[2] Calculated from 3 simultaneous equations for each of runs A, B, and C.
[3] Variously termed "microline," "orthoclase," or "potash feldspar" in the text references. Actually defined as microcline (ref. 2, p. 388), and herein confirmed by infrared as microcline.
[4] For details of determination of An content to ±5% An, see ref. 10.
ND—Not detected at this level of concentration in the sample.

stituent minerals. In Table 1 these results have been compared with the results as given by Chayes (3).

It may be seen that several of the less common components given by Chayes are insensitive to detection by infrared absorption—biotite being one of the most difficult. In mica-rich acid igneous rocks its presence can be detected, but even there its quantification is difficult. Although it may be easily discerned by x-ray analysis, the preferred-orientation problem which is so marked with biotite makes its quantification by x-ray especially difficult.

One of the principal problems encountered in the study of acid rocks is the nature of the potash feldspar. Under the microscope a petrographer usually determines the presence of microcline, by observing the cross-hatched twinning normally associated with this feldspar. The infrared method of analysis, however, indicates the type of potash feldspar by the position and strength of several critical absorption bands. This is illustrated by Figure 2, showing clearly that the potash feldspar in the sample G-1 is microcline and not orthoclase. The critical areas are 13.0, 13.76 and 15.45 microns. While the absorption pattern found for sample G-1 in these regions can be easily accounted for by the presence of microcline, reference to the curve for orthoclase shows that its pattern does not check. At 13.0 and 13.76 microns the orthoclase absorption bands are too broad to account for the resulting absorption bands in the G-1 spectrum, and the absorption band at 15.65 microns is not evident in the spectrum of G-1. Oligoclase (An_{24}) was determined by the configuration of the curve at 9.5–10 and 15.45 microns (10).

To determine further the An content of the plagioclase feldspar, another technique was developed. Instruments of the type used in this study operate on the double beam principle. A synthetic can be used in the second or

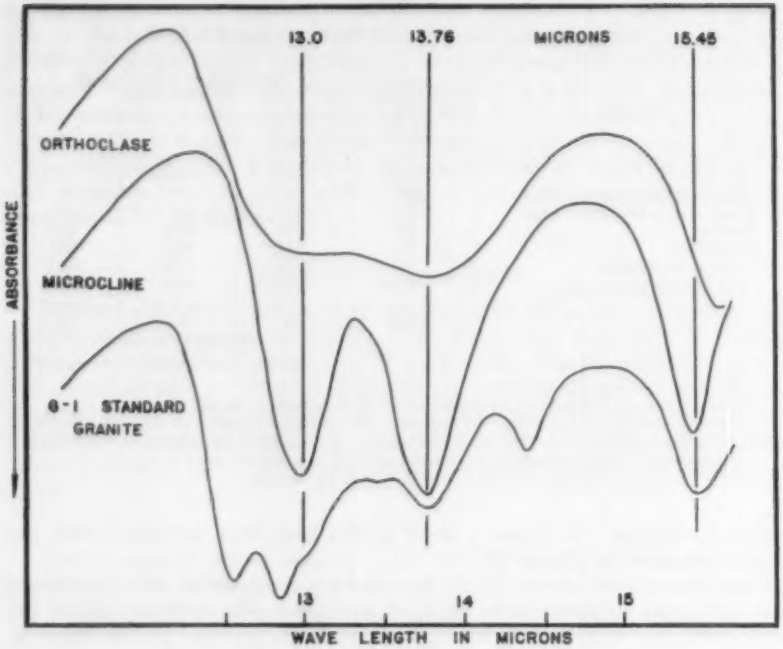

FIG. 2. Detail illustrating the identification of microcline in the standard granite G-1.

reference beam and its absorption pattern will be removed from the final spectrogram of the unknown sample. By simultaneously compensating for the quartz and microcline in G-1, the spectrum of the plagioclase and the remaining minor minerals was more clearly observed. The An content of the plagioclase in G-1 was reaffirmed by this method to be between 26 and 29 percent. By then combining all three major constituents in the reference disc and then obtaining a differential curve with G-1, the spectrum of the low concentration minerals was obtained. While specific determinations of these minor constituents were not made, the resulting curve showed characteristics of muscovite and possibly biotite.

The curves shown in Figure 3 are individual curves for each of the three minerals—quartz, microcline and oligoclase feldspar (An_{26})—indicated by infrared analysis as the predominate constituents in the sample G-1. The critical bands used for the identification and quantification of each of these minerals are circled. The quantification of the three minerals when present together was effected by solving a series of simultaneous equations, determined by their absorption factors at 12.54, 13.48 and 13.76 microns.

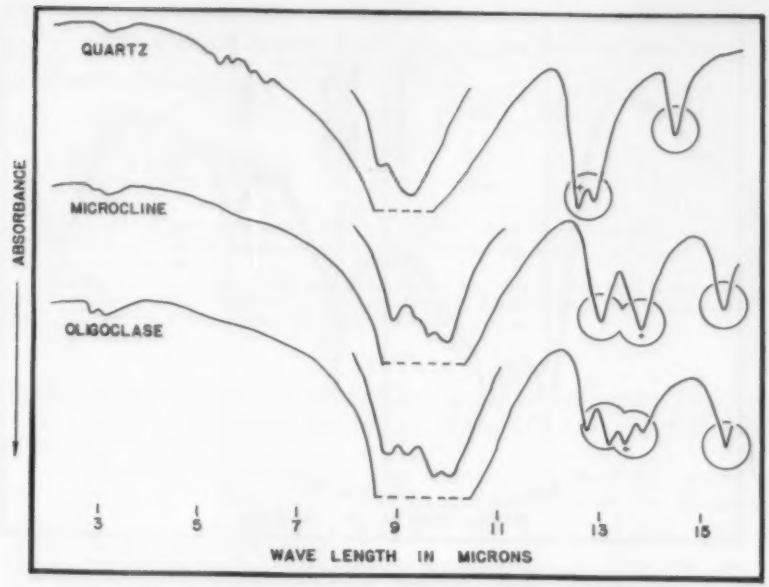

FIG. 3. Absorption curves of major constituent minerals of standard granite sample. Circled areas were considered diagnostic. Bands marked + were used for quantitative analyses.

For the purpose of measurement a "base-line" was drawn tangentially to the points of maximum transmittancy at about 12 microns and 15 microns. The "base-line" absorbancy at any wavelength within this range was considered to be the difference between the absorbancy read from the curve and that read from the line at that wavelength. These "base-line" absorbancies are additive. It was thus possible to follow standard techniques (1, p. 511) and develop equations from which the concentrations of individual components were deduced.

Figure 4 represents the "proof" of the analysis in which an attempt was made to duplicate the curve produced by the sample G-1. Synthetic mixtures containing each of the indicated minerals at their determined levels were made. The curves of the three samples were compared. There is a close similarity between the infrared curve of G-1 and its Research Center counterpart, but an obvious difference in the quartz and microcline contents between both curves and the synthetic as prepared from the previously published data (3).

While we believe that previous results obtained on G-1 are as good as can be determined with the microscope, we feel that the infrared has greater "resolving power" since the measured quantity is a result of interatomic vibra-

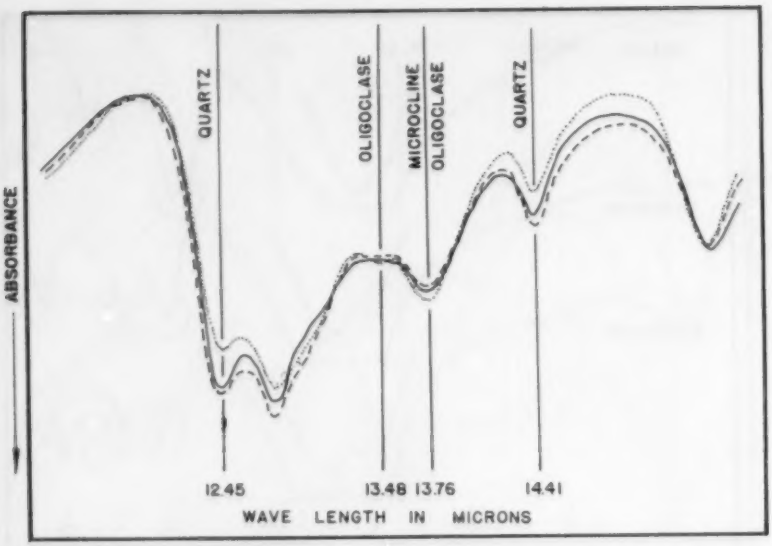

FIG. 4. Comparison of absorption spectra of the standard granite and synthetic mixtures. Solid line, standard granite; dashed line, synthetic based upon KRC analyses; dotted line, synthetic based upon Chayes analysis.

tions within a molecule and is thus independent of particle size. This would be particularly true of sub-micron quartz. A similar condition exists with cryptoperthites in which the plagioclase is below the limit of the microscope resolution.

As far as can be ascertained, the normative composition of the plagioclase in G-1 (3, p. 67) ranges from An_5 to An_{24}. The arithmetic average of the thirty-four values listed in their Table 1 (3, p. 8), was determined to be An_{17}, and this value was used to recalculate Chayes' modal data to yield the partial chemical analysis quoted in Table 2. Chayes (pers. comm.) has indicated that the plagioclase of some samples of the Westerly granite has a composition of An_{22} (Year Book 53, Geophysical Laboratory, 1954, p. 136).

In view of possible determinent errors in the infrared analysis, and the reported variance in the U. S. Geological Survey analysis, the differences between the values calculated from the data of the Research Center, for Al_2O_3 and SiO_2, and the U. S. Geological Survey values are considered to be reasonable. The Research Center findings may have been affected by any one or all of the following:

(a) The Research Center quartz content may be 2 to 3 percent high and the plagioclase may be slightly low (Fig. 4).

(b) In attempting to match G-1, we were restricted by our best available

TABLE 2

PARTIAL CHEMICAL ANALYSES CALCULATED FROM THE PRINCIPAL MINERALS IN STANDARD GRANITE (G-1)

	SiO_2	Al_2O_3	K_2O [1]	Na_2O	CaO
Chayes (3) (An_{12})	71.8	14.2	6.3	3.1	1.1
Research Center[2] (An_{28})	70.3	11.7	5.3	2.0	1.2
U.S.G.S. complete analysis[3]	72.22	14.44	5.51	3.26	1.42

[1] Dana, 4 ed., p. 537, gives 16.0% K_2O in microcline. Soda contents of microcline were not considered, as the assumption of An_{12} above presumes that its soda content was calculated in with the albite content.

[2] Chayes' data for biotite (3.5%) and muscovite (1.4%) content were used to complete the silicate mineral analysis. Biotite composition was calculated from ref. 3, p. 42. About 6.1 weight percent of G-1 is still unaccounted for in the Research Center data.

[3] Table 20, ref. 3.

feldspar sample (An_{28}). A value of An_{29} would be more exact (Fig. 4, at 15.5 microns). This would increase the Al_2O_3/SiO_2 ratio of the Research Center results slightly.

(c) Research Center analyses were insensitive to about 6.1 percent of the total mineral content, even after utilizing Chayes' values for biotite and muscovite. It is reasonable to assume that both Al_2O_3 and SiO_2 might be present in this undetected material.

CONCLUSIONS

If one plots on a triangular graph the quartz content, the orthoclase and the plagioclase feldspar contents, he finds a surprising agreement between the published results and those determined by infrared analysis (Fig. 5). From this figure,[2] we can define the type of rock with which we are dealing based primarily on its *mineralogical composition* rather than upon its texture.

Many of the rocks given to petrologists for identification are altered beyond recognition, but we now have a very powerful tool to aid in the rapid qualitative and quantitative determination of the mineralogy of such rocks. In particular the alteration minerals—kaolinite, alunite, sericite, jarosite, albite feldspar and chlorite—are very sensitive to infrared analysis. It is these minerals that occur in the fine-grained ground mass in so many altered rocks as to make them essentially indefinable to the most competent petrographer.

The infrared analysis method gives an integrated mineralogical composition of samples ranging from a small fragment one milligram in weight, to composites representing many hundreds of feet of drill core.

SUMMARY

A method is indicated by which the quantitative mineralogy of a sample can be quickly, accurately and reproducibly determined by a trained technician, regardless of the degree of alteration or the degree of weathering the

[2] While called a "granite," G-1 actually plots in the quartz monzonite field.

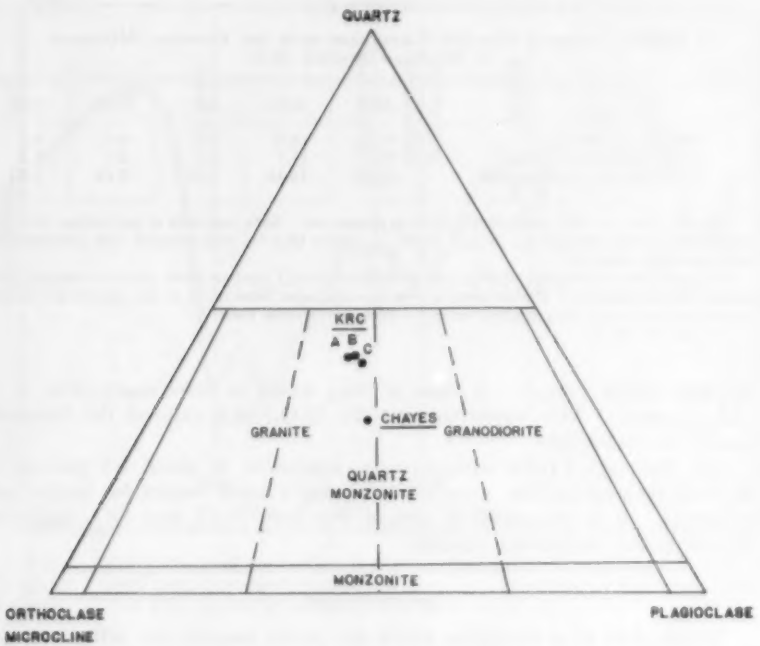

FIG. 5. Triangular diagram showing data of Table 1. Boundaries after Johannsen.

sample has undergone. While it is not possible to determine texture by this method, and thereby deduce the full petrographic history of the rock, this method gives the *present* composition of the rock, and includes a great sensitivity to the minerals formed by alteration or weathering. The results are given in tabular comparison and in graphical form of triplicate sets of runs made upon powdered samples of the standard granite G-1, originally collected and described by the U. S. Geological Survey.

ACKNOWLEDGMENTS

The authors wish to acknowledge the cooperation of H. W. Fairbairn, now Professor of Petrology at Massachusetts Institute of Technology, in originally providing the powder of G-1. The sample was obtained for spectrographic control purposes but has been found eminently suitable for infrared analysis. The consistent care shown by M. C. Randle in the critical field of sample preparation, which resulted in a high degree of reproducibility, is gratefully recognized. They would like to thank S. R. Zimmerley, Director of Research,

for his encouragement of this work, and the Kennecott Copper Corporation for permission to publish the paper.

KENNECOTT COPPER CORPORATION,
WESTERN MINING DIVISIONS RESEARCH CENTER,
SALT LAKE CITY, UTAH,
Nov. 25, 1958

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Economic Geology
Vol. 54, 1959, pp. 1056–1067

SPONTANEOUS POLARIZATION POTENTIALS AND CLAY AND LIMONITE DEPOSITS IN THE GATESBURG FORMATION OF CENTRAL PENNSYLVANIA[1]

GERARDO W. GROSS AND E. JAMES MOORE

ABSTRACT

Geophysical investigation of clay and limonite deposits related to the lower Paleozoic of Central Pennsylvania shows the existence of broad belts of self-potential minima above the outcrops of the Cambrian Gatesburg formation. These S.P. minima are related to the peculiar sandy residual soil covering the Gatesburg. A working hypothesis in terms of shale and liquid junction potentials is advanced to account for the phenomena. This appears to be confirmed by the "mirror image" relationship of S.P. profiles with resistivity profiles. The method may be useful in prospecting for clay deposits and in locating certain geological boundaries.

PURPOSE OF THE INVESTIGATION

THE limonite deposits under consideration were worked for their iron content by open pit operations during the early days of the American iron and steel industry. Renewed attempts at exploitation were undertaken as late as 1942 or 1943 at Scotia when the increasing war-time demand made marginal deposits attractive. The operations proved unsuccessful. Associated white kaolinitic clays, however, are still being worked in a few cases (e.g., the Blair pit, Fig. 1).

The reports of the Second Geological Survey of Pennsylvania (2) mention several instances of pyritic material associated with these limonites. Although considered to be of sedimentary origin by some authors (3), it was conceivable that these limonites in reality are well-developed gossans of (hydrothermal) sulfide deposits, with the primary sulfide zone now weathered to a relatively deep level. If so, one would expect such deposits to be originally made up of a large proportion of pyrite. The possibility of an association of these limonites with hydrothermal sulfides was also suggested by the fact that hydrothermal sulfide veins (pyrite, sphalerite, galena) are known to exist in the area under consideration. For a geophysical investigation of this type of deposit the self-potential technique was chosen since the combination of abundant pyrite (hypothetical) and a well-developed zone of oxidation (as evidenced by the limonites) would cause strong spontaneous polarization. The work described in this paper was carried out to test the above hypothesis.

[1] Contribution No. 58-41, Mineral Conservation Series, from the College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.

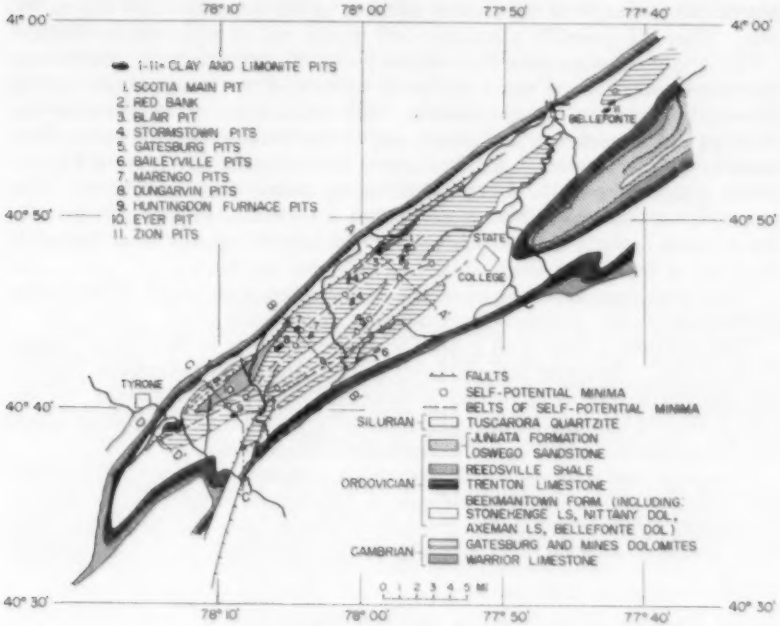

FIG. 1. Geology and belts of self-potential anomalies in the area studied. (Geology based on Geologic Map of Pennsylvania, 1931.)

DESCRIPTION OF THE AREA INVESTIGATED

The most important (but by no means all) of the Central Pennsylvanian limonite deposits are shown in Figure 1, a geological sketch of the area under consideration.

The limonite deposits studied are in a NE trending belt 6 miles wide and 36 miles long, whose axis may roughly be taken as a line through Bellefonte, State College and Tyrone. Geologically, this is approximately the axis of the Nittany anticlinorium of the Appalachian Ridge and Valley province.

There are two shorter zones farther south, of about 12 miles length each: the Roaring Spring and the Woodbury-Williamsburg anticlines, respectively (3). These belong to the same anticlinorium. They contain two of the largest clay and limonite deposits known in the region: Ore Hill, apparently exhausted, and Oreminea, where clay is mined at present.

The belt under consideration is underlain by Cambrian and Ordovician strata (Fig. 1), folded into a series of narrow, subparallel anticlines and synclines shown in the geological sections AA′, BB′, CC′, DD′ (Figs. 2–5). The limonite deposits are generally elongated in a northeasterly direction. Typical dimensions, as deduced fro the pits where they were worked are:

length 300 feet to 1000 feet; width 100 feet to 300 feet; depth 20 feet to 100 feet. They are generally associated with plastic red or white kaolinitic clays.

It is important to note that the majority of these deposits, particularly the largest ones among them, are probably related to the upper part of the Gatesburg or to the Mines dolomite. There are a few to be found in the Warrior and Stonehenge limestones, and in the Nittany and Bellefonte dolomites (e.g.: the Gatesburg, Baileyville and Zion occurrences shown in Fig. 1). Other occurrences in the Devonian Oriskany series were not studied. The stratigraphic relationship discussed implies a structural relationship between the limonite deposits and the flanks of the anticlines; as seen from Figure 1, there are at least three lines of old pits following the flanks.

The weak contrast of relief in the area studied (maximum of the order of 200 feet) makes it especially suitable for geophysical work.

The Gatesburg formation generally is covered by a layer of poor, sandy, residual soil. Outcrops are extremely rare. Detailed stratigraphic correlation without the aid of boreholes is therefore impossible. However, for the sake of brevity the term "Gatesburg outcrop" is used here for the areas where this formation is covered by its characteristic residual soil.

The areas underlain by the Gatesburg are generally characterized by scrub oak forests and brush and an absence of agricultural development. This is a fortunate circumstance as the presence of power lines and other sources of stray artificial currents may severely reduce the utility of a self-potential survey.

METHOD OF INVESTIGATION

The method preferentially applied in this investigation is that of the self-potential traverse. The dimensions of the anomalies discovered as well as the dense brush covering the major part of the interesting areas made it impracticable to realize the original purpose of mapping equipotential lines of individual anomalies. Instead, many roughly parallel traverses were run taking advantage of existing trails. Supplemental studies using resistivity methods were also made.

The apparatus employed consists of a portable Leeds and Northrup potentiometer with a range from 1 to 1,100 millivolts and two copper-copper sulfate non-polarizing electrodes (manufactured by the Georator Corp. of Manassas, Va.).

Polarization of the electrodes was checked by periodically repeating readings with reversed electrodes. This was done at every fifth spacing or wherever a strong reversal of potential occurred. As a rule the electrode polarization did not exceed 0.5 to 1.0 millivolts per electrode. When this happened, the electrodes were either depolarized by mixing their copper sulfate solution in a clean bottle, then refilling them and shunting them together for about 15 minutes in a moist environment, or a fresh pair of electrodes was taken.

Whenever feasible, self-potential traverses were run perpendicular to the structural (NE) trend. The extent of the traverses varied between 1 and 5 miles. The most commonly used spacings were 200 feet and 500 feet. Such

large spacings were necessary because of the large areal extent of the phenomena studied.

According to Jakosky (8), 500 feet is on the average the upper limit of electrode spacing to avoid interference with the locally generated spontaneous potentials by telluric currents. With profiles several miles long it was initially feared that such interferences might become important. However, checking the profiles, or parts of them, with the shorter spacing of 200 feet and rerunning some traverses at different times of the day and year, showed that the phenomena observed are constant and reproducible. Thus the effect of telluric currents may be considered as unimportant.

EXPERIMENTAL RESULTS OF THE INVESTIGATION

The first trial tests showed that self-potential lows exist in the vicinity of known limonite occurrences. They all have some common characteristics, namely: a minimum value 100 to 400 mv below the average regional values, a width of 1,500 feet to nearly 5,000 feet, and a shape only slightly asymmetric (i.e., the gradient on both flanks of an anomaly has approximately the same magnitude).

Characteristic profiles are shown in Figures 2 to 4. The limonite or clay deposits themselves, or what is left of them, are in some cases located on the flank of such a major anomaly rather than near its center. But in other cases they correspond to minor positive peaks near the minimum.

It was thought at first that displacement of the anomaly is due to the dip of the fractures or faults containing the sulfide deposits supposed to exist under the limonite gossan. In an ideal case, the negative center of an S.P. anomaly should be located roughly vertically above the intersection of the ore body with the groundwater level. This is especially true when the ground is flat, as is essentially the case here. If a reasonable value for the dip of the

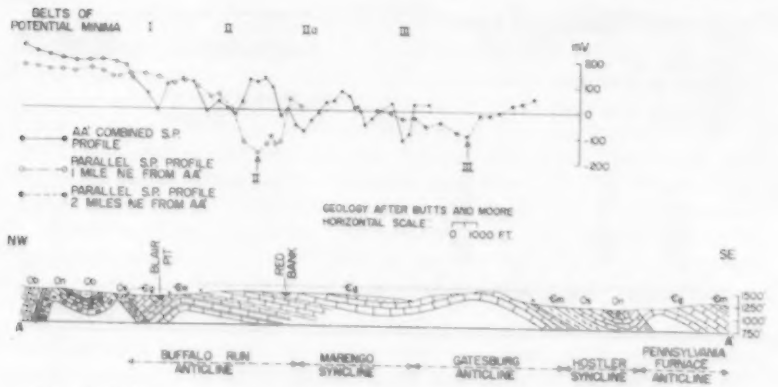

FIG. 2. S.P. and geologic profiles along line AA′ of Figure 1. Geologic legend is on Figure 5.

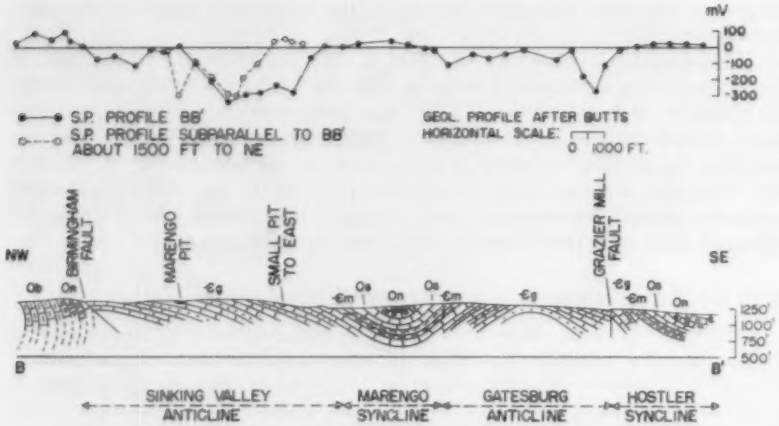

FIG. 3. S.P. and geologic profiles along line BB′ of Figure 1. (See legend of geological symbols on Fig. 5.)

"ore bodies" was assumed it turned out that the displacement was much too big to be accounted for by this hypothesis. Thus, in the case of the Marengo pit shown on profile BB′ (Fig. 3) the displacement of the negative centre from the known occurrence is about 1500 feet in a direction perpendicular to the structure axis, and if the groundwater level were at a depth of 100 to 200 feet the angle of dip of the supposed sulfide zones would have to be 10°

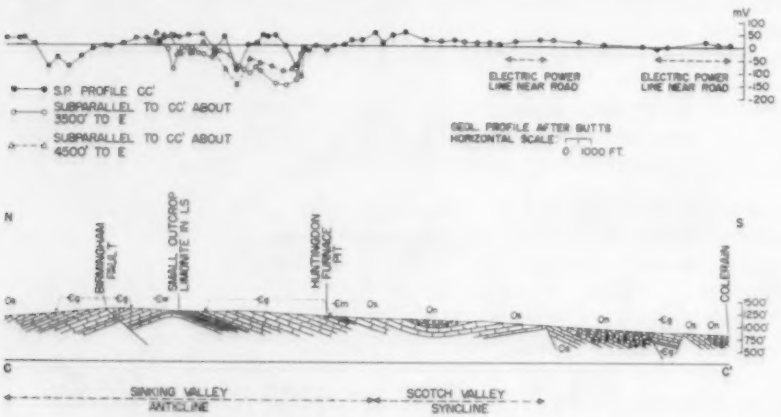

FIG. 4. S.P. and geologic profiles along line CC′ of Figure 1. (Geologic legend on Fig. 5.)

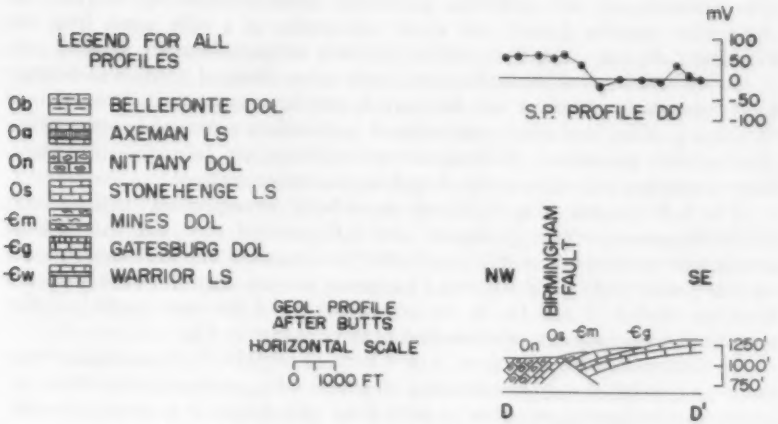

FIG. 5. S.P. and geologic profiles along DD' of Figure 1.

or less. Moreover, the great width and continuity of these anomalies would demand sulfide deposits of improbable dimensions.

Comparison trial profiles were run over known sulfide deposits of the region and the picture obtained was completely different. Three occurrences were studied:

(1) The galena-sphalerite-barite (+ minor pyrite) occurrences near Culp (Fort Roberdeau, Altoona Quad.). No self-potential anomaly was observed.

(2) The Keystone mine, a fissure vein of similar mineralization, west of Birmingham, near Tyrone (Tyrone Quad.). No self-potential anomaly was observed.

(3) A small vein of similar mineralogy but with more abundant pyrite, near Milesburg (Bellefonte Quad.). A potential drop of 240 mv over about 250 feet was observed. The contrast with occurrences (1) and (2), above, may be due either to a greater proportion of pyrite or to more active oxidation and transportation of ions as indicated by a spring near the deposit.

As to occurrences (1) and (2), the mineral association mentioned, with pyrite being scarce, precludes an intensive oxidation with production of appreciable quantities of sulfuric acid, and therefore the complete absence of S.P. anomalies is not surprising. In any case, the self-potential picture of these proven sulfide deposits is quite in contrast with the broad anomalies found in connection with the limonite deposits discussed.

Most of the limonite-clay deposits studied are located in the upper part of the Gatesburg formation. There are some exceptions, all but one of which were investigated. In none of these cases was an association with an S.P. anomaly observed. There is, for instance, a typical anomaly associated with the belt of Gatesburg outcropping between Baileyville and Gatesburg (Fig. 1).

The minimum, of 120 millivolts, is located about 2 miles NNW from the Baileyville limonite deposit and about nine-tenths of a mile south from the Gatesburg deposit. Another profile, run on a subparallel route about 1 mile to the NE disclosed a 150 millivolt anomaly in an identical position in relation to the structure. Thus it was discovered, and later systematically confirmed by many profiles, that there exist belts of spontaneous potential minima rather than isolated anomalies. Without exception, these are related to the Gatesburg formation and, apparently, largely to its upper section.

The S.P. minima (Fig. 1) are in three belts corresponding to three belts of the Gatesburg. The geological and S.P. profiles AA′, etc., as well as others not reproduced in this paper, further illustrate the relationship. As seen in profile AA′ (Fig. 2), belt II appears to split into two closely spaced branches labeled II and IIa in the northern part of the area studied. (For reasons of scale only one of these two belts is shown in Fig. 1.)

In correspondence with these 3 or 4 belts of negative S.P. anomalies there are 3 or 4 belts of clay and limonite deposits. Fig. 1 shows that these deposits may be located on either or both sides of the lines of potential minima. The broad regional character of these belts of S.P. minima is the best proof for the conclusion that they are not associated with small local sulfide deposits.

There are only two instances in which a profile did not show a potential minimum at the theoretical extension of a belt. In both cases the presence of power lines and highly resistive roadbeds are most probably responsible for this apparent irregularity.

The experimental results of this investigation may be summed up as follows:

(1) Three (or four) belts of spontaneous-potential minima were observed, related to the upper part of the Gatesburg formation. They are shown in Figure 1.

(2) Known limonite and clay deposits are located within or on the borders of such S.P. troughs where the deposits are in the Gatesburg formation or the Mines dolomite. The clays (and possibly some limonites) commonly coincide with small positive peaks. Limonite deposits underlain by members of the Beekmantown group (Stonehenge limestone, Nittany and Bellefonte dolomites) do not show association with S.P. anomalies.

(3) Known sulfide deposits in the area have either proved inactive as far as spontaneous polarization is concerned or show (in one instance) a very strong and narrow potential minimum, different in character from the phenomenon described under (1).

(4) The most important regional dislocation, the Birmingham thrust fault, as well as other faults or formation boundaries have no apparent effect on any of the 5 or 6 S.P. profiles crossing them (Figs. 4, 5).

INTERPRETATION OF RESULTS

Several geological structures and processes are known to produce spontaneous polarization resulting in natural earth potentials. An understanding of these is essential in evaluating the significance of the phenomena studied in

this paper. For a discussion the reader is referred to the literature (16, 17, 19).

Natural potentials may be divided into the main groups of electrochemical (or electrostatic) and electrofiltration (or electrokinetic) potentials.

Electrochemical potentials arise: (a) at the interface of electrolytes of different concentrations, different composition or both (liquid junction or diffusion potentials) (12, p. 96); (b) between electrolytes of different concentrations and/or composition separated by some chemically active material such as clay (membrane or Nernst potential, shale potential) (18); (c) at the contacts of solid metallic compounds or metals, e.g., certain ores, with such electrolytes (electrode potentials). Kelly (10) has observed a definite relationship between spontaneous potentials and the pH of the electrolytes generating them.

Electrofiltration or streaming potentials are due to capillary movement of an electrolyte (7, 15, 17).

Of these phenomena, the electrode potential due to oxidation and reduction processes in a weathering sulfide body containing abundant pyrite has already been mentioned and ruled out as a cause of the natural potentials studied in this paper. Liquid junction and shale potentials however (and possibly also electrofiltration potentials) are believed to be of significance.

The Gatesburg formation, as represented in this area, is a cyclical sequence, about 1,700 ft thick, of dolomites and dolomitic sandstones (11). According to a stratigraphic study by C. R. Pelto, it is characterized by a nearly complete absence of shales (he measured 5½ feet). However, a considerable proportion of (13–30 percent) of the detrital fraction of the sandstone members is made up of microcline grains, up to 80 percent of which may be altered to "clay". Limonite patches are common and certain thin dolomite layers contain up to 15 percent of pyrite.

The Gatesburg is covered by a thick mantle (50 to several hundred feet) of sand containing quartzite boulders and fragments of a wide range of sizes, with pockets of clay and limonite. This soil is very characteristic of the Gatesburg formation and is evidently derived from it. The local purity of the three main constituents: sand, clay and limonite, indicates a long period of natural separation and concentration. The clays are believed to be derived from the microcline, and the limonites from the pyrite of the Gatesburg formation as described by Pelto. The possible derivation of some of the limonite from siderite or ankerite has not been investigated.

In some of the known clay or limonite deposits, such as the Marengo pit, described by Butts et al. under the heading of "Furnace Road" (2, p. 107), the pits are water-filled. In this particular instance, the existence of 6 feet of plastic white clay above and 16 feet below the water has been reported by the authors mentioned.

From this description it can be seen that the conditions for the setting up of natural electrochemical potentials exist in the Gatesburg overburden, viz.: clay-sand contacts, and liquid junctions. The working hypothesis which follows is advanced in an attempt to explain the spontaneous potentials observed in terms of the electrochemical behaviour of the geological elements

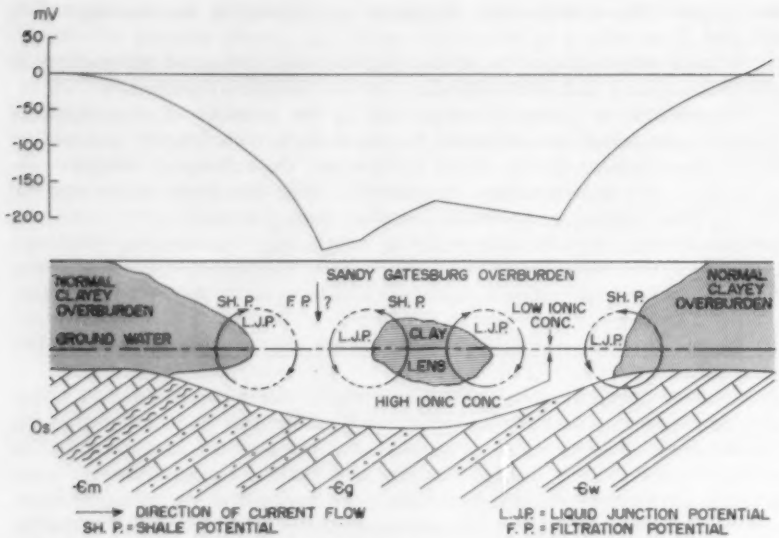

FIG. 6. Diagram for a possible mechanism of generation of the S.P. anomalies described.

described. The diagram of Figure 6 gives a qualitative picture of what is believed to happen. The sandy overburden of the Gatesburg formation in contact with the more argillaceous soils of surrounding formations gives rise to a pronounced negative potential difference between these surrounding formations and the Gatesburg. The reason for these broad negative belts may reside in electrochemical phenomena, such as different ionic concentrations or different values of pH of the interstitial fluids, or in electrofiltration processes, or all of these combined. Clay and limonite pockets within this negative belt give rise to small but nevertheless well-defined positive peaks of the S.P. values. The main electrical activity may occur near perched water tables, but it is well proven that differences of potential may be measured even where a pocket of clay is in contrast with a sandy body high above the ground water level provided clay and sand are damp enough to insure continuous electrolytic interchange. In Figure 6, ground water "level" has been drawn as a horizontal line for the sake of simplicity.

The mechanism of S.P. generation as proposed above is supported by resistivity profiles run along suitable portions of the S.P. profiles discussed. The apparent resistivity was determined by introducing an artificially generated current into the ground by means of two current electrodes and measuring the resultant voltage drop between two potential electrodes. This "four-electrode-configuration" as a whole was then displaced along the profile line so that the relative positions and separations of current and potential

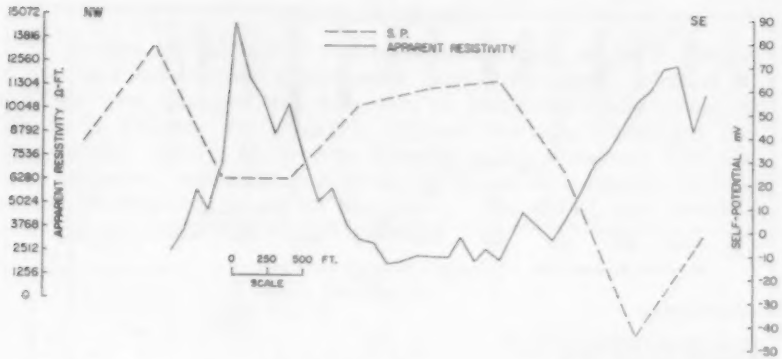

FIG. 7. Spontaneous potentials and apparent resistivities along a portion of the profile of Figure 4. (Line CC′ of Fig. 1.) Wenner configuration with 100 feet spacing between adjacent electrodes was used for resistivity. S.P. spacing of 500 feet.

electrodes remained unchanged. Apparent resistivity was computed from the data obtained and plotted against the position of the midpoint of the configuration. After some trials the most suitable electrode configuration was found to be a "Wenner configuration" with spacings of 30, 50 or 100 feet (8, p. 517). Direct current and commutated direct current sources were both used in different phases of the work, the results being similar in all cases.

If the spontaneous polarization were generated as suggested, one would expect a mirror-image correspondence to exist between S.P. lows and resistivity highs and, conversely, between S.P. highs and resistivity lows. This is precisely what the profiles illustrate (Figs. 7 and 8). The sandy portions of the Gatesburg overburden, characterized by negative S.P. anomalies, show a higher resistance than the clay-rich portions (or the argillaceous overburden of adjacent formations) characterized by more positive values of S.P. On Figure 8, the small positive peak within a broad negative trough (whose SW flank only is shown) corresponds to a clay lens in the sandy Gatesburg overburden. To the southwest, the sandy overburden increases in (disseminated) clay content as the upper section of the Gatesburg with the Orehill limestone member is approached. The strong rise of S.P. and fall of resistivity is characteristic of this geological boundary.

SUMMARY AND CONCLUSIONS

Investigation of residual limonite and clay deposits related to the Gatesburg formation (Cambrian) by the method of natural earth potentials discloses the existence of broad negative potential belts associated with sandy residual soils covering the Gatesburg.

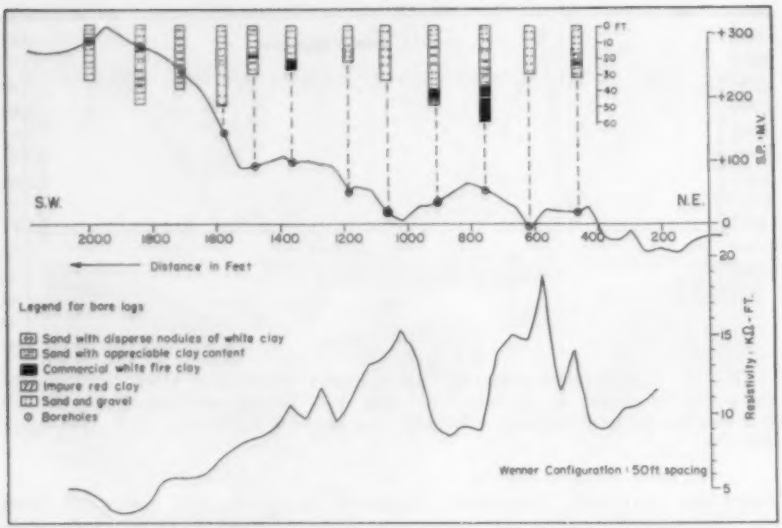

FIG. 8. S.P. and resistivity profile compared with borehole records of the Woodbury Clay Co., Oreminea.

Three and locally four such belts can be distinguished, corresponding to the structural repetition of the Gatesburg by folding.

Clay and associated limonites lie on small positive peaks at the bottom or on the flanks of these S.P. lows.

The negative potentials may be explained in terms of electrochemical processes giving rise to the so-called shale and liquid junction potentials, as opposed to the oxidation-reduction phenomena taking place in and about sulfide ore bodies.

This working hypothesis appears to be confirmed by resistivity profiles. It opens up new possibilities for application of the self-potential method to geological problems. In particular, the method of combined S.P. and resistivity profiles carried out as described has proven useful in the location of deposits of kaolinitic fire clay in the Gatesburg overburden and is expected to work similarly wherever bodies of argillaceous material are surrounded by a sandy matrix as in the cases under consideration. The method also has provided more detailed knowledge concerning the lithologic composition and distribution of the overburden covering the Gatesburg formation.

The method will not work where artificial currents interfere with the natural potentials nor where structures of similar electrical properties are to be differentiated from each other.

The method did not yield useful information when applied to the investigation of known sulfide deposits with one exception or to the location of major faults in the area studied.

ACKNOWLEDGMENTS

The writers are indebted to Professors M. L. Keith and B. F. Howell, Jr. who read and criticized a preliminary draft of this paper. Most of the resistivity work discussed was done with an instrument kindly loaned by Prof. H. L. Yeagley. Dr. Eugene G. Williams was most helpful with geological advice. Mr. J. M. Stevens, manager of the Woodbury Clay Co., kindly authorized measurements to be carried out on the company's land and supplied borehole and geological information. The skilled field assistance of Mr. Joseph Shea is sincerely acknowledged.

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Nov. 17, 1958

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Economic Geology
Vol. 54, 1959, pp. 1068–1077

PHYSICAL AND CHEMICAL PROPERTIES OF THE PETROGRAPHIC COMPONENTS OF A HIGH VOLATILE BITUMINOUS COAL

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ABSTRACT

Concentrates of the petrographic components of a high volatile A bituminous coal were obtained by centrifugal separation in salt solutions of adjusted specific gravity. Samples containing 94 percent vitrinite, 86 percent exinite, 87 percent micrinite, and 96 percent fusinite were obtained.

Various physical and chemical properties of the concentrates were determined, e.g., chemical composition, helium density, surface area, indices of refraction, and X-ray scattering intensities. The components were found to differ considerably in chemical composition and in most of the physical properties. Some of the physical properties could be related to chemical composition.

INTRODUCTION

ALTHOUGH the petrographic components of coal have been observed and described both megascopically and microscopically for many years, systematic determinations of the physical and chemical properties of all of the organic components have been reported only recently. Because the vitrinite and fusinite components (for an explanation of terminology, refer to publications by Berry and Dutcher (3) and Schopf (36)) commonly occur in relatively thick bands or lenses, they can be hand selected in fairly pure form. Various properties of these components have been studied by a number of workers. However, micrinite and exinite occur only in finely disseminated form and their separation is rather difficult. Kröger et al. (15–26), Dormans et al. (8) and Ladam et al (27) have recently separated these components in relatively pure form and have reported results of studies of their physical and chemical properties. This paper describes a study of the physical and chemical properties of the petrographic components of an American coal. The properties investigated are chemical composition, helium density, B.E.T. surface area, reflectivity and X-ray scattering intensities.

EXPERIMENTAL PROCEDURE

A 1½-inch thick layer of dull coal was cut out of a column of Hernshaw bed high-volatile A bituminous coal from Boone County, West Virginia. Thin-section analysis revealed that this layer contained 34 percent spores. The coal was broken in a jaw crusher, hand-crushed to minus 20 mesh, and then ground in a ball mill for 24 hours. After 8 and 16 hours of grinding, material passing a 325-mesh screen (minus 44 microns in size) was removed

to facilitate reduction of the oversize. 94.2 percent of the coal passed this screen at the end of the grinding operation.

The minus 325-mesh coal was immersed in zinc chloride solutions of adjusted specific gravity, in increments of 10 grams in 200 cc of solution, and centrifuged at 2,250 rpm for 10 minutes. The float and sink portions were removed separately, thoroughly washed in distilled water, and air dried. The samples were stored under nitrogen until used for determination of physical and chemical properties.

From a starting sample of 1,200 grams, 110 grams of float on a solution having a specific gravity of 1.25 was obtained. Microscopic analysis showed that this contained 71 percent exinite. This float material was reimmersed in 1.23 gravity solution and yielded 52 grams containing 86 percent exinite. The sink material was placed in a 1.35 gravity solution and the resulting sink was immersed in a 1.45 solution, yielding 58 grams of float containing 87 percent micrinite.

To obtain a vitrinite sample by an equivalent process, 100 grams of a bright layer of the Hernshaw coal was immersed in a 1.25 solution and the resulting sink was placed in a 1.30 solution. The float on the latter, amounting to 63 grams, contained 94 percent vitrinite.

A hand-selected lens of fusain weighing 90 grams was immersed in a 1.45 solution and the resulting sink was placed in a 1.70 solution. The float in the latter, weighing 36 grams, contained 96 percent fusinite.

Vitrinite samples were also selected from this and other coal beds by hand removal of relatively wide homogeneous bands.

For petrographic analysis, briquets were formed by mixing the minus 325-mesh products with melted Lakeside 70 thermoplastic resin and cooling in molds. One surface of the briquets was ground on silicon carbide laps and on a fine Belgian hone. A final polish was obtained with alundum on microcloth. The briquets were examined microscopically using an oil immersion objective and a magnification of 350 ×. Three traverses 20 mm in length were made across a briquet, and the proportions of the components were estimated with a Whipple disc (33). The components were recognized by their relative reflectances because little characteristic structure was observed in the minus 44 micron particles. The observed contents of components in the concentrates from the Hernshaw coal are listed in Table 1.

TABLE 1

PETROGRAPHIC ANALYSIS, BY REFLECTED LIGHT METHOD, OF COMPONENT CONCENTRATES SEPARATED FROM HERNSHAW COAL

Concentrates	Observed contents of components, percent			
	Vitrinite	Exinite	Micrinite	Fusinite
Vitrinite	94	3	2	1
Exinite	0	86	14	0
Micrinite	1	11	87	1
Fusinite	4	0	0	96

The apparatus for determination of helium densities was patterned after that used by Rossman and Smith (35) for carbon blacks. Densities of the components separated in the solutions of different gravity were necessarily measured on minus 325-mesh particles; those of the hand-selected vitrinites were determined on 16 to 40-mesh particles, a size more conveniently handled. An apparently general opinion that helium densities are independent of particle size was confirmed when equivalent results were obtained for minus 325-mesh and 16 to 40-mesh fractions of the same vitrinite. Pretreatment of the samples was required to remove moisture and sorbed gases. The minus 325-mesh samples were initially evacuated in a separate system with accurate control by means of a needle valve to prevent loss of sample. Most of the samples of both sizes were evacuated for 16 hours at a temperature of 60–65° C, after which the pressure remained below 10^{-4} mm Hg with continuous pumping. Helium density measurements were made after a minimum period of 4 hours in contact with helium, little pressure drift occurring after the first hour. The results were corrected for ash content of the coal samples on the basis of volume additivity of coal and ash.

Surface areas of the Hernshaw concentrates were determined by the conventional Brunauer-Emmett-Teller method of nitrogen adsorption at − 195° C.

Reflectivities were measured by the use of a microscope equipped with a vertical illuminator. High magnification (60 ×) objectives, corrected for air, water, and cedar oil immersion, permitted determination of reflectivities in these media. An 8 × ocular was used producing an overall magnification of about 480 ×. A Bausch and Lomb grating monochrometer served as a source. The wave length employed was 5,461 Å. Absolute values of reflectivity in the various media were obtained by comparing photomultiplier photometer readings with those obtained on standard mineral specimens of diamond and calcium tungstate.

X-ray scattering patterns of the Hernshaw components were obtained with a proportional counter X-ray diffractometer, using compressed slab samples. Scattering intensity curves were plotted from counts accumulated over scanning intervals of ½ degree.

RESULTS AND DISCUSSION

The results of chemical analysis of the concentrates of the Hernshaw components and hand-selected vitrinites from this and other coals are listed in Table 2. Also shown are analyses of a Ceylon graphite sample and a resin from a Utah coal, upon which helium densities were obtained for comparison with those of the coal components. Of the Hernshaw components, exinite and fusinite differed most, the former having high volatile matter (55.3 percent) and hydrogen (6.5 percent) contents and the latter low volatile matter (13.4 percent) and hydrogen (3.2 percent). Vitrinite and micrinite contained similar, intermediate amounts of volatile matter (33.7 and 31.4 percent) and hydrogen (5.4 and 4.8 percent). The vitrinite from an anthracite is an example of a very high-rank coal component, with 2.7 percent volatile matter and 1.8 percent hydrogen. The Utah resin is a

TABLE 2

CHEMICAL COMPOSITION AND DENSITIES (BY HELIUM DISPLACEMENT) OF COAL COMPONENTS AND GRAPHITE

	Proximate analysis, percent			Ultimate analysis, percent, M.A.F.					Helium density, g/cm³
	Moisture	Ash	Volatile matter	Hydrogen	Carbon	Nitrogen	Oxygen	Sulfur	
Ceylon graphite		2.9			99.8			.2	2.264
Vitrinite from anthracite, Luzerne Co., Pa.[1]	1.3	1.2	2.6	1.8	95.6	.7	1.4	.5	1.632
Fusinite from high volatile A bituminous coal, Hernshaw bed, W. Va.	.9	3.7	12.8	3.2	91.5	.6	4.3	.4	1.483
Micrinite from Hernshaw coal	1.8	7.9	28.4	4.8	85.9	.7	8.0	.6	1.322
Vitrinite from medium volatile bituminous coal, Indiana Co., Pa.	.8	.9	29.8	5.1	88.0	1.4	4.8	.7	1.281
Vitrinite from Hernshaw coal[1]	1.9	1.4	33.5	5.3	85.8	1.6	6.6	.7	1.291
Vitrinite from high volatile A bituminous coal, Pittsburgh bed, Pa.[1]	1.7	1.8	34.8	5.3	84.1	1.6	8.0	1.0	1.287
Vitrinite from Hernshaw coal[2]	.6	1.8	32.9	5.4	85.2	1.6	7.2	.6	1.281
Vitrinite from high volatile C bituminous coal, Vermilion Co., Ill.	2.2	1.2	45.2	5.7	78.6	1.4	12.6	1.7	1.353
Exinite from Hernshaw coal	.9	3.1	53.2	6.5	86.2	1.1	5.5	.7	1.215
Resin from bituminous coal, Utah	.4	3.6	90.5	10.4	85.6	.4	3.2	.4	1.070

[1] Hand selected from uniform bands.
[2] Obtained from bright coal by gravity separation.

highly volatile component, with 94.3 percent volatile matter and 10.4 percent hydrogen.

The densities of the coal components obtained by helium displacement are listed in Table 2. The sample of Ceylon graphite was included in this series of measurements to test the accuracy of the method. The density of graphite computed from dimensions of the unit cell (2, 28) is 2.24 or 2.28; experimental values of 2.25 were reported by Dulhunty and Penrose (9) and by Van Krevelen and Chermin (39). Thus the density value of 2.264 for Ceylon graphite given in Table 2 agrees very well with reported values.

Specific volumes of the coal components derived from the helium densities are plotted in Figure 1 as a function of the molar hydrogen contents. The data for the Hernshaw components lie on a straight line; extrapolation of the line to zero hydrogen (100 percent carbon) gives a specific volume of 0.43 cm^3/gm, close to that of graphite, 0.443 cm^3/gm. Franklin (12) found a linear relation between specific volume and weight content of hydrogen in coals ranging from 80 to 95 percent carbon but extrapolation of this line gave 0.54 cm^3/gm at zero hydrogen, a value quite different from that of graphite.

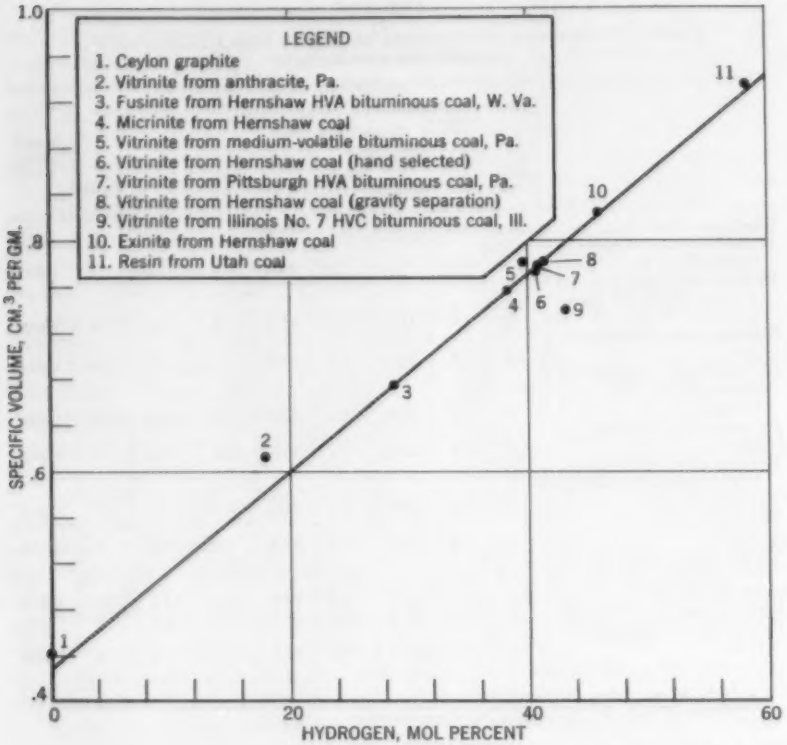
LEGEND
1. Ceylon graphite
2. Vitrinite from anthracite, Pa.
3. Fusinite from Hernshaw HVA bituminous coal, W. Va.
4. Micrinite from Hernshaw coal
5. Vitrinite from medium-volatile bituminous coal, Pa.
6. Vitrinite from Hernshaw coal (hand selected)
7. Vitrinite from Pittsburgh HVA bituminous coal, Pa.
8. Vitrinite from Hernshaw coal (gravity separation)
9. Vitrinite from Illinois No. 7 HVC bituminous coal, Ill.
10. Exinite from Hernshaw coal
11. Resin from Utah coal
SPECIFIC VOLUME, CM.³ PER GM.
1.0
.8
.6
.4
0
20
40
60
HYDROGEN, MOL PERCENT

FIG. 1. Relation of specific volume (measured by helium displacement) to hydrogen content of coal components.

She concluded from this that coals in this range of rank have a similar molecular structure that is not closely related to that of graphite. However, if Franklin's data is plotted on a molar hydrogen basis, the specific volume at zero hydrogen is 0.47 cm³/gm, much closer to that of graphite. Storch (38) pointed out that densities of anthracite, carbon black and meta-anthracite deviate from the linear relationship shown by Franklin but lie on a smooth curve terminating at the graphite value. Van Krevelen and Chermin (39) showed a similar trend of density toward that of graphite when plotted against weight content of carbon.

For a given molecular structure, the molar volume may be considered an additive function of the atomic volumes of the constituent atoms. In a homologous series built up of two kinds of atoms, such as carbon and hydrogen, the molar volume would be a linear function of the mol fraction of either constituent. Although coals also contain oxygen and nitrogen, the total mol

fraction of these elements is small, especially in higher rank coals. The close linear correlation of specific volume with molar hydrogen content for the petrographic components of the Hernshaw coal therefore suggests that coal components have some structural relationship. This result may be unexpected because the petrographic components have different botanical origins or have undergone varying degrees of chemical change during coalification. The deviation from the straight line of the point for the vitrinite from the lower rank Illinois coal may be attributed to its high oxygen content and that of the anthracite to a drift that was observed in helium density measurement. Helium penetrates into anthracites slowly. The agreement of the high hydrogen Utah resin with the straight line relation is noteworthy but perhaps fortuitous.

The nitrogen surface areas of the component concentrates, as measured by the conventional BET method, are listed in Table 3. Considerable controversy has arisen over the interpretation of surface areas of coals as determined by various adsorption techniques. The sorption of nitrogen at liquid nitrogen temperatures was found to be low. Anderson and coworkers (1) have reported the following values for American coals: 7.4 m^2/g for an anthracite, 0.4 m^2/g for a low volatile bituminous coal, 2.7 m^2/g for a medium volatile bituminous coal, 0.4 to 1.5 m^2/g for high volatile bituminous coals, and 1.6 to 3.0 for subbituminous coals. The sorption of polar molecules such as water, alcohols and amines at about room temperature was found to be high, corresponding to surface areas of 50 to 400 m^2/g; the sorption of some other molecules yielded intermediate values (1). Anderson and coworkers, who originally favored the results obtained by nitrogen adsorption, have subsequently concluded that most of the surface of coal as measured by nitrogen adsorption lies in pores with diameters over 200 Å, as nitrogen does not readily penetrate the extensive pore structure in the molecular size range. The present data was obtained to compare the nitrogen surface areas of the petrographic components of a given coal. The data shown in Table 3 indicate that fusinite and micrinite have the largest volumes of relatively large pores (the surface areas being 9.8 and 4.6 m^2/g, respectively) as may also be inferred from microscopic observations. Vitrinite and exinite have about the same surface areas, 2.1 and 2.5 m^2/g, respectively. It should be interesting to see how the sorptive properties of component parts of coals differ when polar molecules are employed.

Indices of refraction were calculated from microscopic measurements of reflectivity in air, water and cedar oil (29). The observed reflectivities and

TABLE 3

SURFACE AREAS OF COMPONENTS OF HERNSHAW COAL AS DETERMINED BY NITROGEN ADSORPTION

Concentrates	Surface area, m^2/g
Vitrinite	2.1
Exinite	2.5
Micrinite	4.6
Fusinite	9.8

TABLE 4

REFLECTIVITIES IN CEDAR OIL AND INDICES OF REFRACTION OF COMPONENTS OF HERNSHAW COAL

Component	Reflectivity in oil		Index of refraction
	Average	Range	
Exinite	0.32	0.29–0.36	1.68
Vitrinite	0.91	0.85–0.99	1.81
Micrinite	1.61	1.38–1.94	2.01
Fusinite	2.65	2.27–3.11	1.91

calculated indices of refraction of the four components of Hernshaw coal are listed in Table 4. The reflectivities of vitrinite and exinite had small variances, while those of micrinite and fusinite covered a much wider range. The reflectivity data reported were obtained from a selection of typical particles of these components. The indices of refraction were calculated from measurements on particles that could be observed adequately in the necessary sequence of air, water, and oil measurements. For this reason, the micrinite index is representative of the top of the range whereas that of the fusinite represents the lower part of the range, probably more properly termed semifusinite. The indexes of exinite and vitrinite are well representative of the narrow ranges covered by these two components. It is not necessary to elaborate upon the differences in the reflectivities of coal components, for this is well known by the petrographers. Nevertheless, reflectivity and index of refraction are important physical properties that bear relation to chemical structure. Presently, it has not been possible to make novel deductions regarding the structure of coal components from the reflectivity measurements alone.

Almost all X-ray scattering investigations of coal have dealt with whole coal samples or with the major, most homogeneous component, vitrinite. A few investigators have presented brief discussions of results on other petrographic components. Kasatochkin (14) described X-ray patterns obtained with spore matter and pointed out that the gamma band at 4.5 Å, observed earlier by Mahadevan (30) and Blayden and coworkers (4) is the most

TABLE 5

DISTRIBUTION OF AMORPHOUS CARBON AND LAYER SIZE GROUPS IN COMPONENTS OF HERNSHAW COAL BY ANALYSIS OF X-RAY SCATTERING IN THE (11) BAND

Group	Atom percent in			
	Exinite	Vitrinite	Micrinite	Fusinite
Amorphous	42	35	15	24
5.8 Å	27	4	—	—
8.4 Å	17	32	27	—
10 Å	10	29	35	60
15 Å	—	—	23	10
20 Å	4	—	—	6

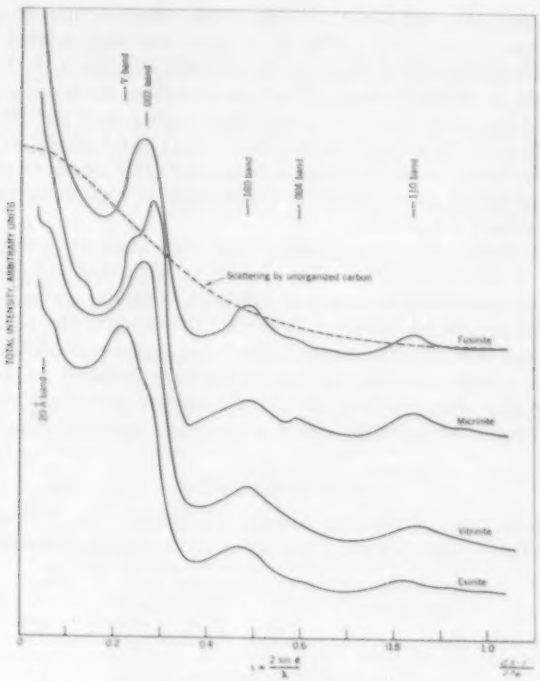

FIG. 2. Intensities of X-rays scattered at different angles by the four major petrographic components of a high volatile bituminous coal.

prominent feature of the exinite pattern. Cartz and coworkers (6) made a similar observation in their study of durains and further stated that micrinite shows scattering similar to that of vitrinite, but with enhanced sharpness of maxima. Cartz et al. concluded that, while the basic aromatic structure is similar in these three components, the packing of aromatic layers is closest in micrinite and poorest in exinite, the latter being affected by the higher content of aliphatic edge groups. Siever (37) and Mahadevan (30) found that fusains gave X-ray patterns similar to but somewhat sharper than those of vitrinite.

The X-ray scattering curves of the four components of the Hernshaw coal are shown in Figure 2. A comprehensive review and assessment of published work on X-ray scattering interpretations of coal structure has been compiled by Ergun and Tiensuu (10). The (002) band, which coincides with the line assigned to the inter-layer spacing of graphite, is believed to result from clusters of parallel aromatic ring layers in coal (13, 32). The (10) and (11) bands are related to carbon atom arrangements in the hexagonal ring structure (7, 13). The gamma band was believed to arise from packings of aliphatic side chains (14) or from irregular packing of buckled

aromatic layers (6). However, recent work showed that it arises from parallel alicyclic layers (11). The 20 Å band has been related to sizes or spacings of scattering units composed of aromatic lamellae (34, 31, 13, 5).

The curves for all the Hernshaw components show the same general structure, with the exception that the gamma band rather than the (002) band is most prominent in the exinite curve. The (002) band occurs as a shoulder on the gamma band, while the latter modifies the (002) peak in the micrinite curve. These are no doubt caused by difficulties in separating these two intimately associated components.

The (11) bands of the components have been analyzed quantitatively by the method of Diamond (7). This technique permitted calculation of the distribution of amorphous carbon and different layer size groups in the components. The results are listed in Table 5. The sizes of the aromatic nuclei are actually less than those shown in Table 5, because in calculating the molecular sizes the innermost atoms of edge groups are included in the layer. It appears that amorphous carbon and smaller groups are characteristic of exinite and vitrinite, while larger layer groups predominate in micrinite and fusinite.

ACKNOWLEDGMENT

The authors are indebted to Conrad F. Matter, Jr., former geologist, Bureau of Mines, who prepared the component concentrates of the Hernshaw coal.

U. S. BUREAU OF MINES,
PITTSBURGH, PA.,
February 23, 1959

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Economic Geology
Vol. 54, 1959, pp. 1078–1093

MANGANESE DEPOSITS OF HUNGARY[1]

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CONTENTS

PAGE
Abstract 1078
Introduction 1079
Geography and physiography 1080
Geology 1080
Urkut 1980
Eplény 1084
Morphology, mineralogy and paragenesis of the deposits 1085
Urkut 1085
Manganese oxide ore 1085
Manganese carbonate ore 1087
Eplény 1090
Manganese oxide ore 1090
Manganese carbonate ore 1090
Origin of the deposits 1091
Historical and statistical data 1092
Bibliography 1093

ABSTRACT

With the exception of one small occurrence, the manganese deposits of Hungary are of sedimentary origin. The two most important occurrences are at Urkut and Eplény, both in the Bakony Mountains of western Hungary. The primary ore in these deposits is of late Liassic age. Two types of ore are recognized—manganese oxides and manganese carbonate.

The primary ore is associated with a typically Alpine facies of Jurassic age. It occurs in a block faulted region, where, in a few places, local folding is also present. As a result of emergence at the end of Jurassic time, the Urkut deposit was exposed to erosion and the primary ore became oxidized and concentrated in a secondary deposit. At Eplény, secondary concentration took place during early Eocene time, also as a result of a long period of emergence and attendant erosion.

The primary manganese oxide ore occurs irregularly as concretions or layers in a variegated clay. The ore minerals are pyrolusite and psilomelane. Two types of primary carbonate ore are present; the "gray" ore contains only rhodochrosite, whereas the "brown" ore contains the rhodochrosite and also manganese hydroxide (vernadite), with goethite in considerable quantity. The host rock of this deposit is a Radiolaria-bearing marl. The secondary, oxidized ore is very clayey and contains detritic material with a low percentage of manganese.

The formation of the oxide and carbonate ores was controlled apparently by physico-chemical differences in the sedimentary basin; the oxide

[1] This paper was presented at the Twentieth Session of the International Geological Congress in Mexico, D. F., in 1956, as a contribution to the Manganese Symposium. The manuscript did not reach the printer's deadline due to circumstances beyond the control of the author.

ore was formed in an oxidizing environment whereas the carbonate ore was formed in a reducing environment, as a result of rhythmic chemical precipitation. The source of the manganese in these deposits was at a considerable distance and consisted probably of a moderately basic igneous or metamorphic complex, which underwent disintegration and leaching, the manganese being transported in solution into the collecting basin.

INTRODUCTION

SEVERAL manganese ore deposits or localities with manganese-rich rocks occur in Hungary (Fig. 1). A few small lentils of oxidized ore are in the epizonal metamorphic complex that makes up the Köszeg Mountains (14). These deposits are probably of sedimentary origin dating back to Carboniferous time, and their mineralogy became quite changed during metamorphism. They have no industrial importance.

All the other manganese deposits in Hungary are related to sedimentary rocks. In the Bükk Mountains near Nekézseny (Fig. 1), manganese-bearing sandstone and shale were discovered during early mining operations. This ore occurrence is also related to Carboniferous sediments. The deposit is insignificant and has no commercial value at present.

In 1952, prospecting was carried on in manganiferous clays that outcrop at several places in the middle Oligocene clay belt for a distance of about 20 km between Demjén and Noszvaj, near the city of Eger (Fig. 1). Core sample examination revealed the primary ore to be composed of manganese

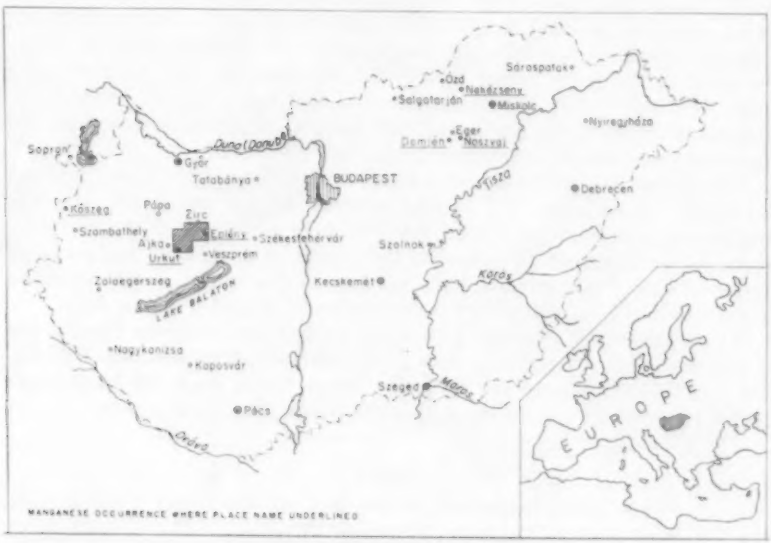

FIG. 1. Index map of Hungary showing manganese occurrences.

carbonate minerals. The finely laminated, gray, $MnCO_3$-bearing marl beds there present contain manganese oxides only in the overlying zone of oxidation.

The most important manganese deposits of Hungary are located in the vicinity of Urkut and Eplény, in the Bakony Mountains (Fig. 2). These ore occurrences are related to lower Jurassic marine sediments. The primary ore was formed during late Liassic time and is at present either in the form of oxide or carbonate. During the emergence, which at Urkut lasted from late Jurassic until middle Cretaceous, and at Eplény until early Eocene, these deposits were partly altered, oxidized, and redeposited in the form of oxides. From an industrial point of view, these two areas represent considerable ore resources and their exploitation has been going on for several decades.

GEOGRAPHY AND PHYSIOGRAPHY

The manganese deposits of Urkut lie in the Southern Bakony range of the Central Mountains of Transdanubia, which extend in the north to the Balaton Highlands. The Eplény deposits, on the other hand, lie in Northern Bakony. The village of Urkut is located at 17°38′E. and 47°05′N., whereas Eplény lies at 17°55′E. and 47°12′N.

Physiographically, the Bakony Range is an ancient massif that was uplifted gradually and exposed to a long period of erosion. Its average elevation at present is between 400 and 550 m above sea level. The region of Urkut appears to be a basin inclined gently to the north, at an elevation of 400 m. The highest point to the south is the basalt mass of Kab Mountain, which is more than 600 m high. Relief over the region is rather pronounced, owing primarily to deep steep-walled valleys that cut into the flat plateau, although gently sloping hills are also present. The principal valleys follow the trend of the faults, which is NW-SE, whereas the less important ones strike NE-SW. With the exception of a few karst springs, there is no permanent stream in the region and rain water accumulates in cavernous and fractured limestone beds at deeper levels.

The Eplény region consists of a broad N-S trending open valley between flat-topped, small hills. Its average altitude is also about 400 m. The neighboring area does not exceed 500–550 m in altitude, with the exception of the Papod Hills, which extend to the southwest and whose highest point reaches 646 m. The physiography of this area is rather monotonous and is characterized by young valleys between a series of gently sloping hills.

The entire region is open to the south toward the Veszprém Plateau and to the north toward the Zirc Basin. The principal valleys run NW-SE. The region is rather arid and the valley floors barely reach the karst water level. Insignificant springs issue from the friable Helvetian gravels.

GEOLOGY

Urkut.—The oldest formations in this area are the Upper Triassic dolomite (Norian) and the Dachstein limestone (Raetian). The Jurassic rocks rest concordantly over the Triassic rocks and their lower contact is grada-

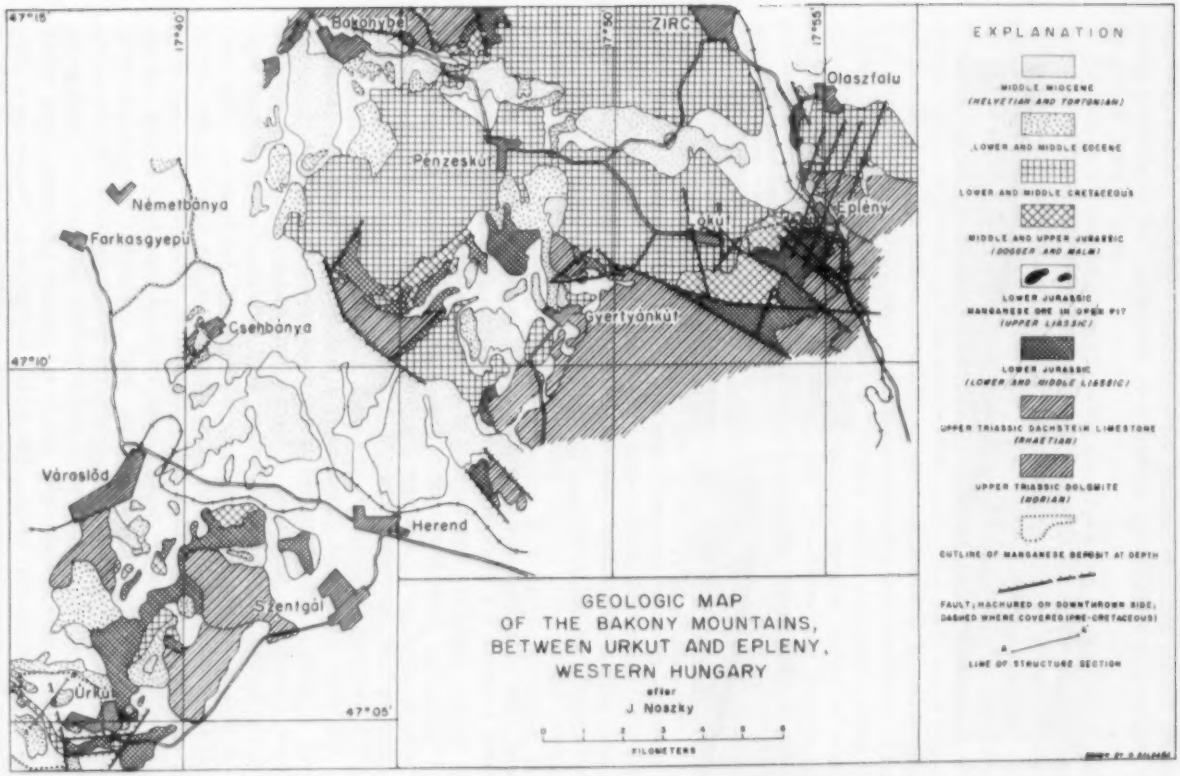

FIG. 2. Geologic map of the Bakony Mountains between Urkut and Eplény.

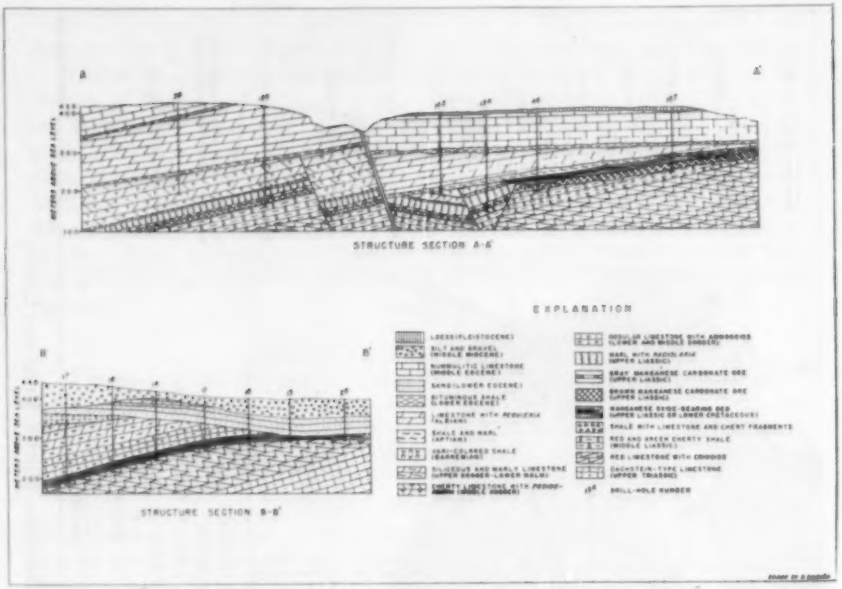

FIG. 3. Structure sections across the Urkut and Eplény districts.

tional from the Dachstein limestone. The lowermost unit of the lower Liassic sequence is a white, yellowish-gray or pink, dense limestone resembling the typical Dachstein limestone. On top of this unit lies a lower Liassic (Lotharingian) dense limestone of red or pink color, which contains cherty beds in its upper part. The next overlying unit is a crinoid- and brachiopod-bearing reddish limestone, resembling the typical Hierlatz limestone that directly underlies the oxide ore at Csárda Mountain (Fig. 3, section A-A').

The most widespread formation is a nodular and cherty red limestone, which contains a rich ammonoid fauna representing the base of the middle Liassic (domerian) sequence. Altered chert nodules are rather common. The top horizon of the middle Liassic beds consists of greenish-gray limestone and marl, which also contain crinoids and brachiopods. This unit generally overlies the carbonate ores, which, in a few localities, are absent and are represented by oxides.

The greater part of the upper Liassic sequence consists of a thick bedded, gray, Radiolaria-bearing, argillaceous marl containing several intercalations of manganese carbonate, or rarely, manganese oxides. The top of the upper Liassic sequence is a brown to purple nodular limestone with light green spots, which passes gradationally into lower Dogger (aalenian) beds, which contain a rich ammonoid fauna. The middle Dogger is represented by a platy and cherty marlstone containing Posidonomya as well as Radiolaria. At Urkut

and in its vicinity, the upper horizons of the Jurassic sequence are not known, owing probably to the continental or terrestrial conditions that prevailed at the end of Jurassic time.

Cretaceous sedimentation began with the deposition of continental beds and with the formation of bauxite and accompanying laterites. Several geologists who studied this area attributed the formation of the secondary manganese oxide ores to this period (23, 29). Unfortunately, however, only the age of the beds that overlie the deposit unconformably can be determined precisely. These beds consist of gray carbonaceous marls, which grade into normal marine sediments of Aptian age. One part of the oxide ore is directly overlain by Aptian argillaceous marlstone containing *Munieria baconica*, which is in turn covered by *Orbitolina*- and *Requienia*-bearing reef limestone. From Albian time onward, the region did not receive marine sediments during the rest of Cretaceous time. Cretaceous sedimentation became limited to bordering or more distant areas, where, during late Cretaceous time, bauxite and coal beds (Turonian), and marine *Hippurites*-bearing limestones (Senonian) accumulated.

Lower Eocene continental clay and bauxite are overlain by gray carbonaceous clay and sandstone, which are in turn covered by *Miliolid*-bearing gray limestone which forms the top of the lower Eocene stage. This limestone grades imperceptibly into a *Nummulite*-bearing limestone sequence of middle Eocene age. From late Eocene until middle Miocene (Helvetian) time, the region was again exposed to erosion, and Jurassic beds, and at places even manganiferous beds, were eroded. During Pliocene time, strong volcanic activity prevailed in the surrounding region, of which the evidence nearest to Urkut is a lobe of basalt covering Kab Mountain, about four kilometers away. The youngest formation is a thin veneer of Pleistocene loess, which covers the entire region.

Structurally, the Urkut area is part of the Bakony tectonic block and is characterized principally by the presence of faults dividing the region into several segments. The general dip of the beds, which is due primarily to tilting, ranges between 20 and 30 degrees, and only rarely reaches 45 degrees. The terrain where the manganese ores occur is highly fractured, and the plastic Jurassic shale and marl beds apparently lent themselves readily to deformation, which resulted in minor folds, faults, squeeze-outs and shear zones. The principal fractures were active repeatedly during the geologic past, yielding to vertical as well as horizontal forces that ultimately produced the structural make-up controlling the present topographic configuration of the area.

The sediments of Mesozoic age accumulated in a branch of a geosyncline or cratosyncline, and they show Alpine characteristics in both lithology and fauna. Early Kimmerian movements are evidenced only by a textural change in the calcareous sediments (oölitic structures) near the Triassic-Jurassic contact, which is interpreted as being suggestive of a gradual rising of the sea bottom. Toward the end of the early Liassic time, another pulse of Kimmerian movements resulted in partial emergence, which dates the beginning of karst development in Csárda Mountain. However, marine sedimentation continued over most of the region and the sea became more wide-

spread by the end of middle Liassic time. During the beginning of this transgression, shallow water sediments accumulated near the margins of the basin, and with progressive deepening of the sea bottom until the end of late Liassic time, sediments of correspondingly deeper water were deposited. This deepening ultimately resulted in a cut-off of water circulation, which in turn caused accumulation of the manganese minerals.

The Dogger sediments are more uniform than the earlier units, as shown by the more homogenous character of the deposits of this age. With the last Kimmerian movements the region became land to such an extent that erosion not only attacked the upper part of the Jurassic beds, but even partly carried away the manganiferous beds or produced in them oxidation and reworking in the eastern part of the Urkut area.

The Barremian sedimentary record evidences local development of bauxite, and with the Aptian transgression the region again was covered by the sea. The Austrian movements produced another emergence, which, in certain basins like that at Ajka (Fig. 1), was accompanied by coal accumulation, while in other basins marine deposition continued during late Cretaceous time. The region where the manganese deposit occurs, with the exception of its marginal areas, remained land from middle Cretaceous until Eocene time. The Laramide movements broke up the terrain into tilted fault blocks. The sea again covered the region during the early part of Eocene time, leaving its marine sedimentary record, and only since late Eocene time has the region been continuously land. During this time the region was affected by repeated movements produced by the Pyrenean, Savian, Styrian, Attican and other deformations, which ultimately gave rise to the present structural configuration of the area.

Eplény.—The structure and geological development of the Eplény deposit show only minor differences from those of Urkut, and, in general, the two areas may be considered to be identical (Fig. 3, section B-B′). The few minor differences present are pointed out in the following paragraphs.

At Eplény, there are small remnants of Liassic Dachstein type limestone present at the base of the manganiferous beds. More commonly, however, the base is formed of the lower Liassic Hierlatz type limestone. Middle Liassic sediments are present only in areas distant from Eplény, a feature that is concluded to mean that the manganese accumulation is of middle Liassic age, or rather that the manganese occurs at or along the middle Liassic horizon. The upper Liassic section at Eplény is considerably thinner than that at Urkut and is represented by Radiolaria-bearing marl on top of which a single layer of manganese carbonate overlies manganese oxide, which is in turn covered by an ammonoid-bearing (*Hildoceras bifrons*) nodular limestone. The lower and middle Dogger sections at Eplény are considerably thicker than those at Urkut, and the rest of the Jurassic sequence is also present. The latter consists of homogeneous, white and pink, porcellaneous and siliceous marl of late Dogger and early Malm age, brownish red *Acanthicum*-bearing nodular limestone of middle Malm age, and reddish ammonoid-bearing limestone and white nodular chert-bearing limestone of Tithonian age.

Early Cretaceous sedimentation continued onward from Jurassic time in the northern and western parts of the Eplény area, but Aptian-Albian sediments are present only in the northern part. The eastern and southern parts were exposed to erosion from late Jurassic until early Eocene time. Locally, just as at Urkut, the manganiferous beds were exposed to erosion and became considerably altered. Lower Eocene sandstone containing manganese and chert fragments directly overlies leached, and clayey manganese ores, which are in turn overlain by middle Eocene Nummulitic limestone, clay and shale. Unlike Urkut, Oligocene sediments consisting of Chattian coal-bearing sandstone and shale are also present in the Eplény region. The lower parts of the area were filled with Helvetian coarse gravel and clayey sand of fluviatile origin, which rest on limestone or directly on leached manganese ores.

Structurally, both the Urkut and Eplény areas are quite similar. The Eplény area, however, suffered minor deformation during the late Kimmerian movements, and instead of the Austrian movements, the Subhercynian and Laramide movements produced important structures. After the Pyrenean and Savian movements, the Eplény area started to sink slowly and to receive marine sediments. Final emergence took place only during middle Miocene time, which was followed by the development of the important faults that are responsible for the present structure of the area.

MORPHOLOGY, MINERALOGY AND PARAGENESIS OF THE DEPOSITS

Urkut

At this deposit, two basically different types of ores are present—oxides and carbonates.

Manganese Oxide Ore.—Manganese oxide ores are in the eastern and southwestern parts of the Urkut district. The following ore types have been recognized:

1—Concretionary crystalline oxide ore
2—Banded and layered argillaceous oxide ore
3—Pisolitic oxide ore
4—Highly argillaceous secondary detrital oxide ore.

The concretionary crystalline oxide ore has irregular distribution and varying thickness. It is found as concretions or nodules of different size dispersed in variegated clays. The diameter of the concretions varies from 0.1 to 1.5 m, being most commonly of fist or head-size. The concretions have concentric structure and are impregnated with silica. Cavities are common in the centers of the concretions, the walls of which are covered with automorphic crystals of quartz and manganese oxide. The outer shell of the concretions is formed of a well defined layer of limonite, which contains no manganese at all. Mineralogically, the concretions consist of an alternation of better crystallized pyrolusite shells with compact psilomelane shells (9, 36).

The banded argillaceous oxide ore is more widespread than the preceding ore and is generally found at the lower horizons of the deposit. Experience

shows that the best quality ore comes from these horizons. The compact, hard layers of ore are separated from each other by thin laminae of reddish-brown, brownish-black, ore more rarely, green clay. Microscopically, the layered ore consists of an intergrowth of fine aggregates and acicular crystals of pyrolusite. The banded ore not only contains pyrolusite, but also manganite and wad. The bands vary in thickness from 5 to 100 mm. The distribution of these ores is also irregular. However, the ore follows more or less the undulating surface of the underlying limestone, and locally, together with the limestone, it shows minor folding; its continuity is interrupted locally by faults of small displacement.

The pisolitic ore type is rather rare in large quantities. It is found generally scattered along the upper horizons of the deposit, in the light colored clays in the form of small pisolites with a diameter of 5 to 20 mm.

The most widespread ore is the highly argillaceous secondary detrital oxide ore which, on the whole, constitutes the part of the deposit that was exposed to partial erosion and is now covered by Cretaceous sediments. A part of the manganese oxide impregnated the accompanying clay, which contains detrital ore fragments of irregular shape and size. Only certain types of this ore can be concentrated by wet processes, and the greater part can not be concentrated by any physical method.

The above described ore types are not separated sharply from each other horizontally or vertically, and they show all kinds of gradations. At Csárda Mountain, for example, the deposit is of the concretionary type and is found

FIG. 4. Old surface workings at Csárda Mountain, near Urkut.

in cavities and sinks in lower Liassic limestone (Fig. 4). Toward the west, in areas surrounding shafts 1 and 2, the ore is of the layered and banded type and is found on the slightly broken-up top of the middle Liassic limestone. In the upper part of the deposit the secondary detrital argillaceous ore is generally present.

It is again pointed out that there is a gradation between ore types and that one type may be present with another in varying proportions.

The host or wall rock in the district is the variegated clay. Its grain size, for the most part, is colloidal and its mineralogy is rather uniform. According to differential thermal analyses (20), the principal clay mineral is illite, with lesser quantities of montmorillonite, kaolinite, and glauconite. Calcite, limonite, and manganese oxides are also present. The color of the clay layers or bands is controlled by the proportion, mineralogical form, and the iron-manganese ratio of the manganese minerals present in the rock. Laminae of white, light yellow, pink, limonite yellow, vermillion, green, brown, black, and gray colors alternate with each other.

According to β-ray tests, radioactivity appears to be the highest in the compact, fragmental, and concretionary ores, while the carbonate ores and their accompanying clays show 30 to 50 percent less radioactivity. The sediments directly overlying the deposit proved to contain only a minimum amount of radioactivity (19).

Manganese Carbonate Ore.—In the western part of the Urkut district the manganese ore occurs exclusively in carbonate form. However, toward the south, southwest and east, both oxide and carbonate ores are found. The relationship between them is as follows:

1. In the southwestern part of the district the carbonate ore is below the oxide ore; both ores are in upper Liassic beds. The original Jurassic cover is missing and the immediately overlying rocks are Aptian sediments, which cover the deposit unconformably.
2. In the southeastern part of the district the carbonate ore is above the oxide ore, both being in middle Liassic beds. The overlying Jurassic beds are mostly intact, with the exception of the immediate surroundings of shaft 1, where Aptian sediments also cover the deposit.
3. In the northern part of the district the relation between the oxide and carbonate ores is not clear, due to the fact that the zone of contact between these two ores coincides with a fault. At this locality, drilling has shown that the oxide ore alternates with the carbonate ore, and also that the deposit is in upper Liassic beds. Lacking extensive mine workings, the composition of the transition zone is not yet known in detail.

Thus, the carbonate ore is everywhere an upper Liassic marine deposit, and with its good stratification and fine banding indicate rhythmic precipitation. It is about 10 to 15 ms thick in the western part of the district. Near its margins the deposit splits into wedges and becomes thinner, particularly where it is in contact with the oxide ore.

Megascopically, the ore is seen to fall into two basic color groups, com-

posed of alternating bands of grayish white, yellow, purple, pink, brown, light green, dark green and black. These two color groups are the "gray" carbonate ores and the "brown" oxi-carbonate ores. This distinction is also reflected in the mineralogical composition of these ores.

The "gray" carbonate ore is mostly light in color and is banded with grayish white, gray, pink, or light-green layers of clay. It consists of a very fine grained, dense, marl-like material with porous earthy texture or with a harder banded structure. Microscopically, the ore is made up of small homogenous carbonate grains, which are angular or slightly rounded and fit together in a mosaic pattern. A small amount of clay impurity is also present. Some beds of this ore contain scattered or disseminated specks of "bacteriopyrite," or tiny hexahedral pyrite crystals. Larger pyrite nodules (20–50 mms) also occur. The ore mineral is rhodochrosite, which is present in separate crystals not intergrown with calcite or siderite (20). Calcite generally replaces skeletons of organic remains or fills the cracks. The other accessory minerals are flaky, fine-grained glauconite and illite. Heavy mineral analyses show that muscovite, biotite, and dolomite make up less than one percent of the total. In the upper part of the deposit the phosphorus content (14–22% P_2O_5) well exceeds the average 1 to 2 percent. X-ray examination shows that these layers contain very fine-grained fluorapatite. A curve depicting the results of a differential thermal analysis made of a "gray" carbonate ore sample is given in Figure 5.

The "brown" oxi-carbonate ore varies from light brown to dark chocolate brown and even to black, with intervening, very thin, light-gray or pink bands or lenses. The ore is dense and is colloidal in grain size; its general composition is that of a clay-marlstone. Microscopically, it is heterogenous and has a lenticular structure with light-colored carbonate lenses, laminae and concretions, all of which are in a highly argillaceous, translucent reddish brown colloidal groundmass. The ore minerals are rhodochrosite, an amorphous hydrate of manganese oxide which is probably vernadite ($MnO_2 \cdot nH_2O$), and goethite. The iron content is higher than that of the "gray" ore. Pyrite and siderite are completely absent, but small quantities of calcite are present. The most important clay mineral is illite. Brown glauconite, muscovite, and barite are also present in small quantities. In comparison with the "gray" ore, the "brown" ore has a minimum content of sulfur and phosphorus, and in well separated samples the brown layers contained no phosphorus at all.

Both types of ore, particularly in the lowermost and uppermost parts of the deposit, contain turquois-green clay bands of varying width, which consist almost entirely of glauconite (20). Figure 5 gives the results of differential thermal analyses of the brown oxi-carbonate ore.

The host rock accompanying both the carbonate and oxi-carbonate ores is a gray, finely banded Radiolaria-bearing marl, which contains calcite, and smaller quantities of kaolinite and illite. Galuconite and dolomite are also common (20). Among the heavy minerals, muscovite, biotite, and limonite are present in small quantities. The marl near the deposit contains small

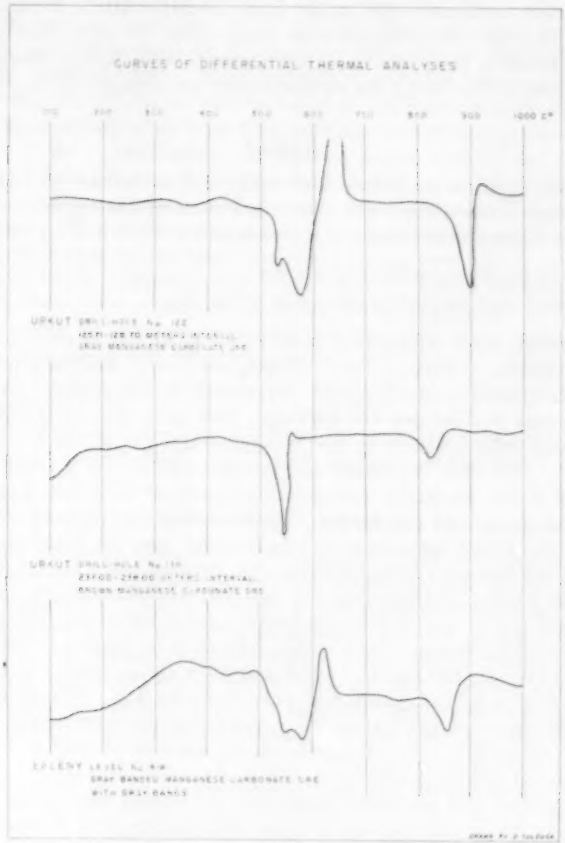

FIG. 5. Curves of differential thermal analyses of carbonate ores from Urkut and Eplény.

percentages of manganese carbonate, but farther away its manganese content does not exceed 1 to 2 percent. Locally, marl beds are exposed on the surface, where, as a result of disintegration, their manganese and iron minerals altered to oxides; the calcite was leached away and the upper part of the marl sequence was altered to a light-yellow clay with veinlets of limonite and manganese oxide.

	MnO_2	MnO	Fe_2O_3	FeO	SiO_2
Urkut—Oxi-Carbonate ore	9.7	24.0	8.7	—	17.7
Urkut—Gray Carbonate ore	—	18.6	1.4	10.1	21.5
Urkut—Mn Carbonate ore	—	23.7	13.0	1.7	25.3

The Urkut carbonate ores range from 18–24% MnO, 8–10% Fe, and 22–25% SiO_2; the oxi-carbonate ores range from 10–21% MnO_2, 13–24% MnO, and 18–20% SiO_2; the oxide ores carry 0–41% MnO_2, 30–65% MnO, 4–5% Fe, and 3–4% SiO_2; the rhodochrosite ore contains 50% MnO.

Eplény

At Eplény, just as at Urkut, both oxide and carbonate ores are present.

Manganese Oxide Ore.—The oxide ore occurs in the southern and eastern parts of the Eplény district and is represented by the following two types:

1. Concretionary crystalline oxide ore,
2. Layered and banded argillaceous oxide ore.

The concretionary ore appears to be identical to that in the Urkut district and is not further discussed here. Pyrolusite is the dominant ore mineral, with smaller quantities of manganite, cryptomelane, psilomelane, and limonite.

The layered and banded ore alternates with very thin layers of soft clay, whose stratigraphic relation to the concretionary ore shows no orderly arrangement. This clay is present in various parts of the district, locally in the form of a flat, elongated, discontinuous body, or as a thin layer between the black manganiferous clay layers. Because of its soft disintegrating nature, it is not suitable for mineralogical examination, and its mineralogical composition is not known. Quantitatively, the concretionary ore is more abundant in the Eplény district than the layered ore. The oxide ore rests on the karst surface of the underlying lower Liassic limestone, filling its topographical irregularities and more or less following its surface. The dominant host rocks of the district are the yellow and black clays, which are sporadically accompanied also by red, green and gray banded clays. The principal minerals of the very soft and plastic clays belong to the montmorillonite group (Fig. 5). Some iron and manganese oxides are also present and even small lenses of pyrite and rhodochrosite occur in the black clays.

In the eastern and southeastern parts of the Eplény district the oxide ores were exposed to weathering and erosion, and during early Eocene time they were reworked. The secondary ore complex consequently is considerably different from the primary ore. The deposit is characterized by a great dispersal of the manganiferous material and the ore fragments or few concretions are distributed in the highly colored clays without any orderly arrangement. Apart from the limestone and chert fragments, big blocks of limestone (1–2 m), fine quartz sand and fine gravel are found in the beds of variegated clay. The grade of the ore is necessarily lowered and the clay components are increased. The upper part of the deposit is poorly stratified and grades into the overlying lower Eocene sand and sandstone beds.

Manganese Carbonate Ore.—Manganese carbonate ore is found in the western and northwestern parts of the Eplény district. It belongs to the upper Liassic sequence, occurring generally above the oxide ores or independently from them. In the northeastern part of the district extensive mine workings provide sufficient data to show that the oxide and carbonate ores

have a facies relationship according to which they may grade into each other vertically as well as laterally. It so happens that carbonate ore develops from black clay that overlies or accompanies the oxide ore through a regular and natural interfingering. Most commonly, however, the overlying black clay becomes gradually more calcareous and passes into the Radiolaria-bearing marl sequence, having at its base thin intercalations of manganese carbonate. The ore is of the "gray" type. At Eplény, unlike Urkut, the ore consists exclusively of light-gray marl-like layers which are separated from each other by dark-gray layers of clay, which contain less manganese and more calcite than at Urkut. The calcium-manganese ratio is commonly one to one. The clay minerals belong to the montmorillonite group and pyrite is commonly present with them. Crystal clear fragments of quartz, sparse glauconite grains, and silicified or calcareous skeletons are all present.

On the whole, the carbonate ores are well stratified, finely layered, lenticular marine deposits of late Liassic age, which were formed during quiet conditions of deposition under a reducing environment. The host rock is a radiolaria-bearing marl.

The Eplény carbonate ores carry from 10–14% MnO, and the oxide ores 23–34% MnO_2, 8–10% MnO, up to 36% Fe_2O_3, and 14–18% S_iO_2.

ORIGIN OF THE DEPOSITS

From the foregoing discussion it appears that both at Urkut and Eplény the manganese deposits are of sedimentary origin and are related to Jurassic marine sedimentation. The formation of the manganese ores began toward the end of middle Liassic time and lasted until the end of late Liassic time, as shown by the rhythmic accumulation of the oxide, oxi-carbonate and carbonate ores, and finally the carbonate ores, together with the accompanying sediments. Both oxide and carbonate ores are typically marine precipitates, a conclusion supported by the mineralogy of the ores and the presence of fossils.

The ore facies varies in accordance with the physico-chemical changes that occurred in the sedimentary environment. Near shore, where good aeration persists, strong oxidation took place and caused precipitation of oxides of manganese and iron due to the controlling effects of the Mn^{+4} ions. In off-shore areas, where oxidation is less effective and where Mn^{+3} and Mn^{+2} ions are equally stable, both oxi-hydroxides (oxi-carbonate ore) and carbonates were precipitated. In the deepest, least agitated part of the basin, under reducing conditions in the presence of carbon dioxides, hydrogen sulphide, phosphoric acid and other products of decay, the manganese carbonate complex formed with a high rhodochrosite, pyrite, and glauconite content. The major part of the iron entering the sedimentary basin was precipitated near shore, whereas the manganese remained in solution and was mostly deposited in the center of the basin in the form of carbonate. At Urkut, for example, the total metallic manganese content of the carbonate ore amounts to five times that of the oxide ore, while the iron content of the carbonate ore is barely half that of the oxide ore.

The direct relationship of the oxygen content of the sea water to the velocity of water circulation is evidenced by the oxide ore complex in the eastern part of the Eplény district, where large pieces of silicified tree trunks were found, and by the oxi-carbonate ores, from which carbonatized fossil plants were collected from small lenses. These organic remains were brought into the basin by a rapidly flowing stream whose water must necessarily have contained large quantities of oxygen. The sudden change in sedimentation at the end of middle Liassic time is also supported by the heavy mineral residues, which in the uppermost middle Liassic marls and cherty limestones are principally of metamorphic or basic magmatic origin (kyanite, garnet, actinolite, amphibole, biotite, muscovite, tourmaline, titanite, zircon, epidote, zoisite, staurolite, diopside, tremolite, anthophyllite, rutile, augite and corundum). Minerals of sedimentary origin, however, are also present (dolomite, limonite, chlorite, glauconite, apatite and barite). The light fraction contains, besides skeletal remains, sparse quartz grains and moderately basic feldspars.

In contrast to the above, the upper Liassic ore complex, together with the Radiolaria-bearing marl shows a complete absence of metamorphic minerals in the heavy mineral residues, and the overwhelming presence of autochthonous minerals is apparent. The most common minerals are pyrite, limonitic glauconite, green glauconite and limonite. Less common are barite and dolomite. Minerals of magmatic origin are muscovite and biotite, both in very small quantities. The light fraction contains, besides chalcedony and dolomitized skeletal fragments, sparse grains of quartz.

The data cited above provide the only basis on which to establish the origin of the manganese ores, for no rocks are known at the surface or at depth, either nearby or far away, to which the origin of the manganese may be attributed. The above minerals indicate that during Jurassic time, metamorphic and basic igneous rocks were exposed at the surface at a considerable distance, and that the manganese was derived from the erosion of these rocks. Detrital minerals make up only a fraction of one percent of the entire rock, a fact which suggests that most of the elements were carried into the basin in solution and were there precipitated by chemical processes.

HISTORICAL AND STATISTICAL DATA

In the area bordering the village of Urkut, manganese ores have been known for a long time from surface outcrops. However, the mining of this deposit was started as a result of geological exploration in 1917, in search of the extension of coal beds from the Ajka basin, when the sinking of an inclined shaft near Csárda Mountain into the lower Eocene coal beds unexpectedly cut a manganese oxide body 5 m thick. The production of manganese from the Urkut district in 1954 was about 250,000 tons.

At the beginning, exploitation was centered on ore bodies that occupied karst sinks in Csárda Mountain (Fig. 4). These ores were concentrated by handsorting. Later, with the exploitation of the layered and detrital argillaceous ores, mining operations extended underground and the ores were

concentrated mechanically by washing. Production progressively changed from east to west with the sinking and deepening of shafts 1, 2, and 3. Exploratory drilling started in the years 1917–1920 and has continuing up to date with varying interruptions. More than 150 holes were drilled in the district, of which two-thirds proved to be productive. The carbonate ore was recognized during 1953–54 (23), and mining commenced after completion of a well planned exploration and drilling program and after solving the problem of concentration.

In the Eplény district, exploration started in 1928 after a manganese ore outcrop was noted on the surface. Development of the deposit started with the sinking of exploratory shafts, and oxide ore has been produced since 1932. The production in 1954 was about 30,000 tons. At the beginning, exploitation was carried on in an open pit. Later, however, adits, inclines and finally a large vertical shaft facilitated mining the dipping ore body. Due to the relatively shallow nature of the Eplény deposit, drilling was less important than at Urkut. A total of 31 holes were drilled, of which 20 gave good productive results. The grade of oxide ore produced during the years has remained more or less the same and, consequently, the technology of its extraction has not changed. The ore can be used without concentration. The secondary ore, which was developed in 1956, consists of detrital argillaceous manganese ore which, in years to come, just as at Urkut, will be concentrated by washing. The carbonate ore, owing to its low grade, has not yet been mined at Eplény.

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Jan. 5, 1959

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* Work published only in Hungarian.

Economic Geology
Vol. 54, 1959, pp. 1095-1102

THE ALTERATION OF ILMENITE

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ABSTRACT

The alteration of ilmenite in air due to oxidation at elevated temperatures has been studied. The final product of oxidation at 850° C was found to be a mixture of hematite, pseudobrookite, and rutile in an approximate molar ratio of 1:5:7. This product is almost identical with naturally occurring "brown leucoxene." At lower temperatures (650° C) a mixture of hematite with probably some rutile and as yet unidentified phase was obtained. From color changes as well as from thermogravimetric analysis, it was observed that slow oxidation could take place at temperature of even 100° and 200° C. The oxidation products were weakly paramagnetic and for products heated for equal periods, the susceptibility decreased with increasing temperature of oxidation.

INTRODUCTION

LEUCOXENE is believed to be an alteration product of ilmenite and hence as a continuation of the X-ray study of natural leucoxenes (4) it was decided to study the alteration of ilmenite under controlled conditions.

Previous Work. Ramdohr (7) in 1943 and later Overholt, Vaux and Rodda (6) in 1950 found from X-ray powder patterns that ilmenite when heated overnight in air at 900° yielded pseudobrookite and rutile.

In 1954, Curnow and Parry (2) studied the high temperature oxidation in air of ilmenite from the beach sands of Australia by magnetic and X-ray methods. They observed that on heating between 600–800° C the magnetic susceptibility was enhanced and the X-ray powder photograph was describable as a "set of lines which were indistinguishable from the lines of the original fraction and of lines due to rutile." Mineragraphic examination also showed no difference between the original and heat-treated grains. Prolonged heating at temperatures above 800° C resulted in the production of a weakly ferromagnetic material with a volume susceptibility almost the same as the original ilmenite. The Debye-Scherrer X-ray pattern of this material was resolved into a set of rutile lines and a set of lines due to a tet agonal crystal with lattice parameters a = 4.861 Å, c = 6.625 Å, c/a =r1.363.

In 1956 Bailey, Cameron, Spedden and Weege (1) studied by optical and X-ray methods the alteration of ilmenite taking place naturally in beach sands. They have recognized three stages of alteration (a) Patchy ilmenite, in which there are patchy intergrowths of altered and unaltered ilmenite, (b) Amorphous iron-titanium oxide or a mechanical mixture of amorphous TiO_2 and iron oxide; and (c) leucoxene, in which all grains identified optically as leucoxene proved to be (by X-ray analysis) finely divided rutile in the

form of oriented crystalline aggregates, except one that was found to be an oriented aggregate of brookite.

Procedures Followed.—The ilmenite grains used as the starting material were obtained by hand picking the impurities from the commercial grade 1 ilmenite concentrate produced in the industry at Quilon, Kerala State, India. The X-ray pattern of these corresponded to that of pure ilmenite.

Small quantities of the finely ground (less than 325 mesh B.S.S.) ilmenite were heated in an electric oven at 650° and 850° for various periods and then air quenched. The former temperature was specially selected in view of the interesting results previously obtained (2). The temperatures were maintained constant within ± 10° C.

The X-ray powder diffraction patterns of the samples were obtained generally on the Phillips wide-angle diffractometer at a scanning rate of ¼° or ½° 2θ/minute using filtered CuK_α radiation. In certain cases the patterns were also photographed in a standard G.E. powder camera with filtered FeK_α radiation.

The magnetic susceptibility was measured using a Guoy-type balance at a field strength of 3,000 oersteds.

To study the weight changes taking place at various temperatures a thermogravimetric curve up to 1,000° C was recorded on the Stanton recording thermobalance of 1 mg sensitivity.

THE OXIDATION OF ILMENITE

Oxidation at 650° C.—Samples were heated for 24 and 72 hours. In both cases the color was completely altered from black to dark brown, and the X-ray patterns even with FeK_α radiation, were rather faint and diffused, indicating the crypto crystalline nature of the products. The first few d-spacings as obtained on the diffractometer are tabulated and compared with those of the original ilmenite and a standard hematite in Table 1.

It is evident that the patterns of both the heated samples do not correspond to ilmenite as found by Curnow and Parry (2) but are essentially that of hematite with probably a very small amount of rutile. The product at this stage was definitely different from that obtained by them, because not only did it differ in the X-ray pattern but also in the magnetic susceptibility, which was found to be 28.32×10^{-6} c.g.s.u. at 29°, considerably less than that of ilmenite (1×10^{-4} c.g.s.u.).

The pattern of sample B (heated for 70 hours) has three additional lines at 3.385, 2.871, 2.428 Å, which cannot be attributed to any known compound of iron and titanium oxides.

From the small difference in the two patterns it is assumed that within 24 hours a definite stage of alteration was reached and that the additional lines of sample B were due to better crystallization of the unknown phase or phases present. The products at this stage could roughly correspond to the second stage of alteration-amorphous iron-titanium oxides, as suggested by Bailey et al. (1).

Oxidation at 850° C.—Ilmenite was heated at this temperature for periods of ½, 1, 2, 4, 6, 24 and 48 hours and air quenched. From the X-ray

TABLE 1

D-VALUES OF OXIDATION PRODUCT AT 650° C

Sample A heated 650° 24 hours		Sample B heated 650° 70 hours		Hematite A.S.T.M. card No. 6-0502		Ilmenite A.S.T.M. card No. 3-0781		Ilmenite original	
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0
3.68	20	3.68	30	3.68	70	3.73	50	3.72	60
—	—	3.39	10	—	—	—	—	—	—
3.23	10	3.23	10	—	—	—	—	—	—
2.87	10	2.87	20	—	—	—	—	—	—
2.69	100	2.69	100	2.69	100	2.74	100	2.74	100
2.50	80	2.50	80	2.51	80	2.54	85	2.53	80
—	—	2.43	—	—	—	—	—	—	—
2.19	50	2.19	50	2.20	70	2.23	70	2.23	60
—	—	2.11	—	2.07	10	—	—	—	—
1.833	40	1.835	40	1.837	70	1.86	85	1.86	60
1.686	80	1.690	80	1.691	80	1.72	100	1.717	80
—	—	1.632	10	1.634	10	1.63	50	1.627	40
—	—	—	—	1.596	40	—	—	—	—
1.481	20	1.479	25	1.484	70	1.498	50	1.496	—
1.446	20	1.448	25	1.451	80	1.462	50	1.444	75

patterns it was observed that after 6 hours no further changes took place. The X-ray patterns of the samples heated to less than 6 hours were generally weak and also more or less similar to each other except that intensities of a few lines increased with the time. Rutile was present even in the sample heated for ½ hour, and the amount progressively increased as the heating was continued. Pseudobrookite lines were detected only in the samples heated for 1 hour or more. Of the ilmenite lines, only the 100 intensity line at 2.74 Å, which is very close to the 80 intensity line of pseudobrookite, was detected in all these samples, but its intensity did not alter eitherway on increasing the time of heating. The other strong lines of ilmenite could not be detected even in the sample heated for ½ hour. This absence is considered to indicate that the ilmenite lattice was almost completely disrupted or very severely distorted even on heating for ½ hour at 850° C. Besides the lines attributable to rutile and pseudobrookite, these also contained the same additional lines at (3.38 and 2.88 Å) observed in the samples heated at 650°. The phase or phases, which constituted these X-ray lines, could not be identified.

The pattern of the samples heated for 6 or more hours were quite sharp and could be identified as due to pseudobrookite and rutile, with probably very small amounts of hematite. Apart from the probable presence of hematite, the main constituents were unmistakably pseudobrookite and rutile as previously reported (6, 7). Curnow and Parry (2) had reported that under these conditions ilmenite oxidized to rutile and another phase, the X-ray pattern of which was resolved as due to a tetragonal lattice with $a = 4.861$, Å and $c = 6.625$ Å. Since they have not published the observed d-values and as no space group was mentioned by them, the d-spacings for the various planes of such a unit cell were calculated for all hkl values

TABLE 2

COMPARISON OF D-VALUES OF PSEUDOBROOKITE AND OF THE UNIT CELL SUGGESTED BY CURNOW AND PARRY (2)

Pseudobrookite				d-spacings calculated after Curnow and Parry (2)	
A.S.T.M.		Synthetic			
d	I/I_0	d	I/I_0	d	hkl
4.96	33	4.902	45	4.86	100
3.48	100	3.483	100	3.44	110
2.74	80	2.748	80	2.74	102
2.45	13	2.454	20	2.43	200
2.40	11	2.402	25	2.38	112
		2.221	10	2.28	201
2.20	11	2.198	15	2.20	003
1.97	24	1.971	25	1.95	212
1.86	27	1.862	30	1.86	113
1.74	13	1.744	15	1.72	220
1.66	5	1.663	15	1.65	004
1.63	8	1.632	20	1.62	300
1.54	53	1.540	35	1.54	310

ignoring the space group extinctions. These are compared with the pseudobrookite d-spacings (Table 2).

From the small differences it is considered likely that the other phase observed by them was actually pseudobrookite and that therefore their

TABLE 3

ALTERATION OF ILMENITE
d-values of ilmenite heated 850°, brown leucoxene and 1:5:7 mixture
(first 15 lines only)

Ilmenite heated 48 hours		1 $Fe_2O_3 \cdot 5\ Fe_2O_3 \cdot TiO_2 \cdot 7\ TiO_2$ mechanical mixture		Brown leucoxene hand picked (from photograph)		Remarks
d	I/I_0	d	I/I_0	d	I/I_0	
4.89	45	4.90	45	4.89	50	Pseudobrookite
3.68	9	3.68	7	—	—	Hematite
3.48	100	3.49	100	3.48	100	Pseudobrookite
3.24	80	3.24	80	3.24	100	Rutile
				2.86	5	
2.75	85	2.75	80	2.75	80	Pseudobrookite
2.69	20	2.69	27	2.69	10	Hematite
2.51	15	2.51	20	2.51	6	Hematite
2.49	50	2.48	40	2.49	60	Rutile
2.45	30	2.45	20	2.45	40	Pseudobrookite
2.40	30	2.40	25	2.40	25	Pseudobrookite
2.30	20	—	—	—	—	
2.22	15	2.22	19	2.22	25	
2.20	30	2.20	30	2.20	60	Hematite
2.19	35	2.19	35	2.19	60	Rutile
1.97	30	1.97	25	1.97	60	Pseudobrookite

results are not in any way contradictory to those of Ramdohr (7), Overholt and associates (6) or the present authors.

It was also observed that these patterns were almost identical in every way with those obtained previously (4) for "brown leucoxene" (Table 3).

Since brown leucoxene was considered to be a mixture of hematite, pseudobrookite and rutile in the approximate molar ratios of 1:5:7, respectively, a corresponding artificial mixture of pure α-Fe_2O_3, Fe_2TiO_5 and TiO_2 was prepared. This artificial mixture is referred to in all subsequent discussion as the 1:5:7 mixture. The X-ray pattern of this mixture is also tabulated in Table 3. From the near-identity of these patterns it is obvious that ilmenite oxidized at 850° for 6 or more hours was almost the same as "brown leucoxene" or the 1:5:7 mixture.

The diffractometer tracings of the oxidation products indicated that hematite was most probably present in small amounts. This was confirmed from the following experiments.

Leaching by HCl.—The amount of Fe_2O_3 leached out by HCl of a particular concentration in a fixed time would depend upon whether only pseudobrookite or pseudobrookite and hematite were present in the oxidation product. Accordingly 20 mg of the oxidation product (24 hrs), 20 mg of the 1:5:7 mixture and 12.5 mg of pseudobrookite were each treated with 20 ml of 1:1 aqueous solution of pure HCl and the mixture digested on a water bath for 6 hours. The amount of iron leached was determined in the filtrate colorimetrically using the thiocyanate method, with the Hilger Spekker Colorimeter. 12.5 mg of pseudobrookite were purposely taken to equal the weight of pseudobrookite in 20 mg of the 1:5:7 mixture. The duration was fixed from separate experiments on the solubility of hematite in 20 ml. of 1:1 HCl. The results of the duplicate experiments so made, are:

Oxidation product—3.1 ± 0.1 mg Fe_2O_3
1:5:7 mixture—3.5 ± 0.1 mg Fe_2O_3
Pseudobrookite—1.7 ± 0.1 mg Fe_2O_3.

The results showed that approximately the same amount of Fe_2O_3 were leached from the oxidation product and the 1:5:7 mixture, thus implying the close correspondence of composition.

Twenty mg of the 1:5:7 mixture contained 1.7 mg of Fe_2O_3, 12.5 mg of Fe_2TiO_5, and 5.8 mg TiO_2. Subtracting the amount leached from 12.5 mg. of Fe_2TiO_5, from the total amount of Fe_2O_3 leached from the 1:5:7 mixture, on excess of 1.8 mg Fe_2O_3 is found. This agrees well with the original amounts of free Fe_2O_3 present. Similarly, in the case of the oxidation product, an excess of 1.4 mg of Fe_2O_3 is obtained. This is taken to indicate the presence of 1.4 mg of free Fe_2O_3 in 20 mg of the oxidation product, i.e., roughly 7 percent of free hematite.

Magnetic Measurements.—The magnetic susceptibility of ilmenite was found to decrease with increasing temperature of oxidation. The susceptibilities of the oxidation product obtained at 850° and 24 hours and the 1:5:7 mixture were nearly identical:

Ilmenite heated 650°, 24 hours	28.3×10^{-6} c.g.s.u.
Ilmenite heated 850°, 24 hours	22.8×10^{-6} c.g.s.u.
1:5:7 molar mixture	22.6×10^{-6} c.g.s.u.

From these results it was concluded that:

(a) ilmenite when heated at 850° for 6 or more hours was oxidized to a mixture of hematite, pseudobrookite, and rutile in the approximate molar ratio of 1:5:7, respectively, thus:

$$12FeTiO_3 \xrightarrow[6\text{ hours}]{850^\circ} Fe_2O_3 + 5Fe_2TiO_5 + 7TiO_2. \qquad (1)$$

(b) the oxidation product so obtained was very similar to brown leucoxene.

Oxidation from 30° to 1,000° C.—While complete change in the color and also the structure took place at both the higher temperatures studied, slight change in color was observed even at 200° in about 20 days. Thus slow oxidation at slightly elevated temperatures as found on the tropical beaches could occur in a few hundred years.

To ascertain the weight-changes at various temperatures, a thermogravimetric record was obtained (Fig. 1) at a heating rate of 300° per hour. Small but distinct increase in weight was noticeable even at 100°, though

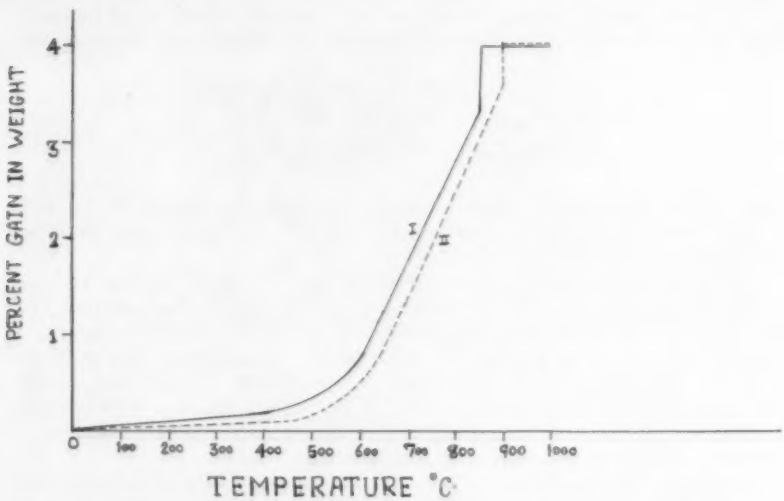

Fig. 1. Thermogravimetric curve of weight gained by ilmenite on heating to 850° C, maintaining at that temperature for 1 hour and subsequent further heating to 1,000° C. (I) 300 mesh material (II) 200 mesh material.

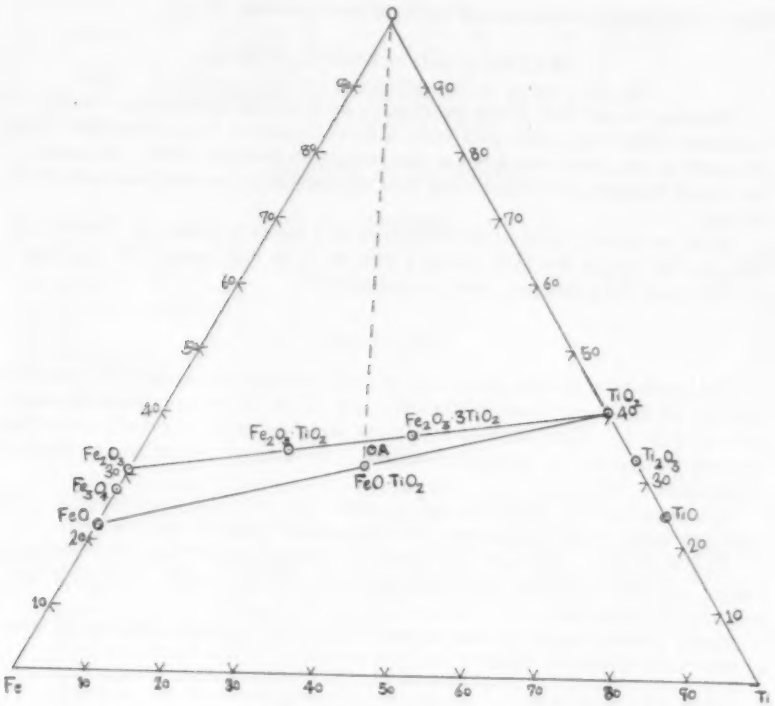

FIG. 2. The ternary diagram Fe-Ti-O. "A" represents composition of 1:5:7 mixture in weight percent.

the increase was more rapid after 500°. On maintaining the temperature at 850°, constant weight was obtained after a half-hour. No further increase in weight was observed when the heating was continued for 1 hour or when the temperature was raised to 1,000° C. Under these conditions a total gain of 4.0 percent in weight was observed as against the 5.2 percent to be expected if equation 1 was obeyed. This could be due to the fact that gain is very slow during the last stages.

GENERAL REMARKS

The oxidation results obtained above are considered as representing most probably, conditions of metastable or non equilibrium. The oxidation of ilmenite under equilibrium conditions can be regarded as movement along the tie-line $FeTiO_3$-O in the system Fe-Ti-O (Fig. 2). If the oxidation had reached the Fe_2O_3-TiO_2 tie-line, it is clear that, under equilibrium condi-

tions, only pseudobrookite and rutile should co-exist (5) as,

$$2FeTiO_3 + \tfrac{1}{2}O_2 = Fe_2TiO_5 + TiO_2.$$

However, since the X-ray pattern of an artificial equi-molar mixture of pseudobrookite and rutile had very different relative intensities than those obtained in the patterns of either the oxidation product (850°, 24 hours) or the 1:5:7 mixture, it is considered that the oxidation product was not on the tie-line.

If the oxidation product is considered as a point in either the FeO-Fe_2O_3-TiO_2 or the larger Fe-Ti-O ternary system it is not impossible for Fe_2O_3, Fe_2TiO_5 and TiO_2 to exist even in equilibrium.

CONCLUSIONS

The oxidation of ilmenite in air at high temperatures (850° C) yields a mixture of hematite, pseudobrookite, and rutile in an approximate molar ratio of 1:5:7. This product is almost identical with naturally occurring "brown leucoxene," a naturally occurring alteration (weathering) product of ilmenite.

At lower temperatures of about 650° C a mixture of hematite with probably some rutile and an as yet unidentified phase is obtained.

The oxidation products are weakly paramagnetic and for products heated for equal periods the susceptibility decreases with increasing temperature of oxidation.

From color changes it was noted that oxidation had commenced even at 200° C in about 20 days.

CHEMISTRY DIVISION,
ATOMIC ENERGY ESTABLISHMENT TROMBAY,
BOMBAY, INDIA,
Oct. 20, 1958

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Economic Geology
Vol. 54, 1959, pp. 1103–1114

A BERYLLIUM DETECTOR FOR FIELD EXPLORATION[1]

GEORGE M. BROWNELL

CONTENTS

	PAGE
Abstract	1103
Introduction	1103
Geophysical equipment	1104
Assaying	1109
Exploration	1112
Acknowledgments	1113
References	1114

ABSTRACT

The portable instrument, here referred to as a "berylometer," is a new geophysical tool for the use of the geologist in both exploration and examination of beryllium deposits. This is a scintillation counter which contains a phosphor having a high neutron to gamma ratio of detection and makes use of the $Be^9(\gamma,n)Be^8$ reaction. A gamma emitting source is carried in a shield on the bottom of the instrument which, when set upon any beryllium-bearing mineral or rock, causes the emission of neutrons from the beryllium which are immediately recognizable. Gamma rays are biased out and neutrons only are counted. An automatic counting register records the neutron count and since this is directly proportional to the beryllium content of a sample, a simple means of analysis is provided.

The use of beryllium would expand rapidly if adequate reserves could be established and also if, with increased production, a lower cost could be attained. The discovery of non-pegmatitic deposits offers a better prospect for the development of substantial reserves in contrast to the generally small size of beryllium-bearing zones as found in pegmatites. Towards this end the Berylometer provides a much-needed field instrument for all persons engaged in the search for beryllium ore.

INTRODUCTION

THE amazing advances in nuclear physics during the past decade and the application of this new knowledge to the development of nuclear power, has created a demand for elements previously little known or, until recently, of minor industrial significance. Since these elements must be obtained from the earth, the problem of discovering new and more adequate sources is a constant challenge to the economic geologist.

Currently one such problem is the discovery of more abundant reserves of Beryllium, which is an element possessing a number of peculiar qualities

[1] Presented at the St. Louis meeting of the Society of Economic Geologists, November, 1958.

that give it an importance in nuclear reactor construction as well as a potential value in high speed aircraft, missile and space ship development. Beryllium is a steel-gray metal with a specific gravity of only 1.874, being the lightest metal having substantial strength. It has a melting point of 2343° F. As an alloying metal with copper, nickel, and others, beryllium generally imparts an ability to be hardened on heat treatment and a resistance to corrosion. As an oxide it is a refractory with high thermal conductivity; and either as the oxide or in the metallic form it is a moderator and a reflector of neutrons. This latter property makes it highly desirable as a shield surrounding the core of power reactors, its primary purpose being the reflection of neutrons from the chain reaction back into the core, thus preventing the loss of power. This reduces the number of fuel rods needed and increases the efficiency (1, 2).

Present inadequate supplies of beryllium are obtained largely from the one material "beryl." To date, most production has come from pegmatite dikes where it is commonly restricted to certain zones. In places it occurs in distinctive green hexagonal crystals that are easily recognized, but elsewhere it is yellowish or even white and may so resemble quartz or feldspar as to be readily overlooked. Also there are other beryllium-bearing minerals, relatively uncommon so far as now known, occurring under geological conditions that have not yet been given adequate attention. Apart from the difficulties of recognizing many beryllium minerals at sight, chemical assays for this element are difficult and expensive and very frequently erratic in their results (7). In the routine analysis of rocks, any beryllium that may be present is most likely included with the aluminum unless special care is taken to effect the separation of the two elements. These factors have all contributed in maintaining beryllium as a relatively costly metal but despite the cost the recent nuclear power and missile developments have created a demand for this important element. A special effort is now required in order to locate more adequate sources of supply and towards this end the author believes a much greater attention should be paid to non-pegmatitic beryllium occurrences as a possible solution to this present problem.

GEOPHYSICAL EQUIPMENT

A new portable field instrument, the "Berylometer," (3) has recently been developed and this promises to be of much assistance in the field for both exploration and examination of beryllium deposits. It makes practical use of a well-known nuclear reaction to detect the presence of beryllium in rocks or specimens, and provides a rapid method of assaying. When beryllium in any chemical combination is bombarded by gamma rays having an energy higher than 1.66 Mev, photoneutrons are emitted in the following reaction:

$$Be^9 (\gamma,n) Be^8$$

The source of gamma radiation employed in the Berylometer is Antimony 124, a pile produced radioisotope with a sixty day half-life. About 76 percent of its gamma radiation is above the 1.66 Mev activation energy necessary to bring

about this transmutation (1). Deuterium is the only other element in the periodic table that undergoes a similar (γ,n) reaction with natural or artificially activated radioactive sources. Other gamma-neutron reactions require gamma ray energies such as may be produced only by accelerators. Deuterium occurs in only trace amounts in water, however, and the threshold of gamma radiation necessary to bring about the emission of neutrons from deuterium is 2.23 Mev which is higher than the radiation given off by Antimony 124. Consequently, the production of neutrons from beryllium is specific with this equipment, there being no reaction from any other element to confuse the operator.

The form of the Berylometer is illustrated in Figure 1. It is a scintillation counter incorporating a 5-inch photomultiplier tube and phosphor, the latter being an enriched boron polyester-zinc sulphide disc that has a high neutron detection efficiency, about twice that of the enriched BF_3 tube commonly used in neutron detectors. Although the BF_3 tube may possess a superior neutron : gamma discrimination ability, the geometry of the disc type of detector

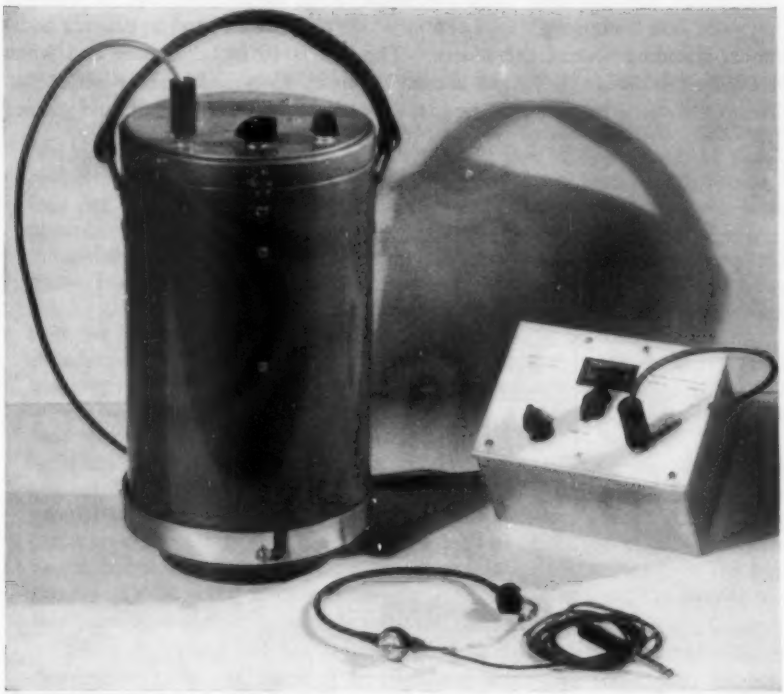

FIG. 1. The portable Berylometer for field exploration with earphones and impulse counter.

is very much better suited to the construction of a portable field instrument. An Antimony 124 source sealed in a metal capsule is fixed in a cavity on the lower side of a lead shield that is attached to the base of the instrument while it is in operation, as shown in Figure 2. When the instrument is not in use, this shield is detached and deposited in a lead "castle" that conforms to safety regulations.

As a safety measure, the Berylometer is suspended from a pole about eight feet long carried between two men during normal field use, as in Figure 3. By this means the operators maintain a safe distance from the source whose gamma radiation is directed downwards. The instrument can readily be set down on any rock outcrop and the presence of beryllium detected immediately by means of ear phones worn by the rear man who directs the work. However, for quantitative measurement or for assaying of samples, the earphones are replaced by a small portable counting register that automatically records the neutron count. The total weight of the instrument is 10 pounds and with shield attached as carried in the field is about 25 pounds.

The "castle" is a separate unit that houses the shielded source when the instrument is not in use. The unit used by the writer consisted of a strong plywood box containing a lead cup in which the shield rested to provide additional shielding around the source. The box is 10 inches square and when the shield is inside, it weighs a total of about 75 pounds. In practice one leaves the castle in camp, in the car, or whatever vehicle is used, and carries

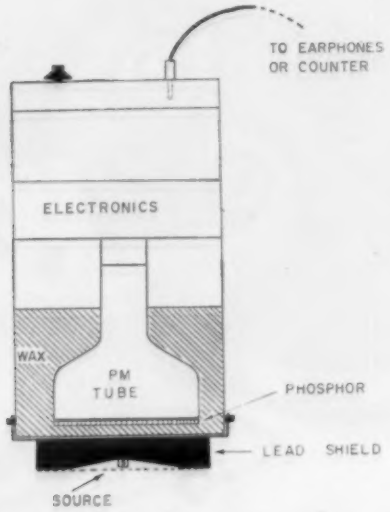

FIG. 2. Diagram showing the relative position of the major components of the portable Berylometer. The lead shield carrying the radioactive source is detachable from the base of the instrument.

FIG. 3. The Berylometer is carried by two men in normal field operations. The rear man is using earphones.

the instrument with the shield attached to the site of operations whenever this involves travel on foot.

There is only one discriminator control knob for operating the instrument, besides the on-off switch, and it is set at a point just beyond where the gamma rays from the source are cut off or reduced to a background count of three or four per minute. This can be accomplished because the scintillations in the phosphor caused by the gamma rays from the Antimony 124 source are less intense than those caused by neutrons. Consequently, the smaller electrical pulses from the photomultiplier tube due to gamma ray activity can be biased out by the use of a suitable discriminator in the electronic circuit and hence only the larger pulses due to the neutrons remain to be counted.

Figure 4 is a graph on semi-logarithmic scale showing on curve A the counting rate of the gamma rays at different settings of the bias control obtained when the instrument had a 46 millicurie Antimony 124 source attached ready for operation but no beryllium present.

Then when the instrument was lowered upon an 80 gram sample of 10 percent BeO, counts were again taken. By subtracting the gamma background from the total for each position, respectively, the resulting neutron count was derived as shown by B. For normal operation, then, the discriminator dial should be set in this instance at a point about 76 where the background gamma count is only 4 and the neutron count from the beryllium in this particular sample is just above 800 counts per minute.

Since Antimony 124 has only a 60 day half life, its gamma radiation will decrease steadily and curve A in Figure 4 will move steadily to the right. Replacing the 46 millicurie source by another source of only 12 millicuries changed the position of curve A to A^1 and this resulted in a corresponding

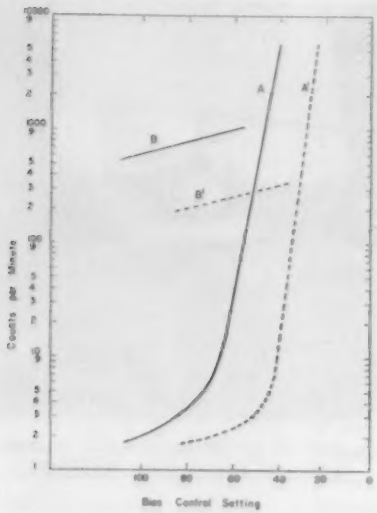

FIG. 4. A. Gamma background count from a 46 millicurie source of Antimony 124. B. Neutron count, less background, from an 80 gram sample containing 10% BeO with the 46 millicurie source. A′ Gamma background count from a 12 millicurie source of Antimony 124. B′ Neutron count, less background, from an 80 gram sample containing 10% BeO with the 12 millicurie source.

decrease in neutrons from the beryllium in the sample. But when one set the discriminator to a position where only 4 gamma counts per minute were obtained from the 12 millicurie source, and the instrument again placed upon the 80 gram sample of 10 percent BeO, instead of obtaining a count of about 200 neutrons as would be expected, the count was actually slightly above 300. This must result from a considerably smaller pile-up of gamma rays in the phosphor from the weaker source, which permits a lowering of the discriminator level with consequently a higher neutron detection efficiency.

The fortunate increase in neutron detection efficiency as the Antimony 124 source loses strength extends the useful life of the source considerably. This should permit a source starting at 80 millicuries to give good performance for at least two half lives or for four months in a portable field instrument, though the requirement of the individual operator will determine how much lower it may be permitted to go and still remain useful. It is obvious that the safety factor afforded by the lead shielding becomes greater as the strength of the source declines but this should not lessen the operator's awareness that he carries a dangerous product. There will be times when he must hold the instrument by hand against a sloping surface or even the vertical walls of an underground mine, but the duration of such action should be made as brief as possible. The wearing of a film badge for measuring exposure to radiation

is a requirement for any person possessing the necessary license to use a radioactive source and this may be worn at about ankle height.

When the Antimony 124 is to be replaced in the shield, it is shipped in its castle to the supplier where the spent source is replaced by a fresh source, the operator thereby being relieved of any responsibility for handling or disposing of the radioisotope.

ASSAYING

The use of $Be^9(\gamma,n)Be^8$ reaction to determine the beryllium content of a sample is not new. Pannell and Freyberger (4), (5) used radium and Antimony 124 sources of about 1 curie strength to detect as little as 1 milligram of Be in ore. By this means also they developed an automatic picker to remove small pieces of beryl from a moving belt.

This scheme was further developed by Gaudin and Pannell to permit analyzing quantitatively for beryllium. Using an Antimony 124 source of about one curie strength and a large sample, they could detect 1 to 2 parts per million of beryllium. A recent paper (6) describes the use of the (α,n) reaction employing polonium as the source. In each of these methods boron tri-fluoride tubes were used to measure the neutron count.

The neutron count obtained from a sample is directly proportional to the beryllium content. A simple comparison in counting rate between a standard and an unknown sample of similar weight and geometry will determine the beryllium content of the latter. The author uses a flat metal 2-ounce ointment can of about 2.5 inches diameter and .75 inch thick that holds 80 gram samples, and also the 4-ounce size. Standards having 1, 5 and 10 percent beryllium oxide were prepared by thoroughly mixing the required proportions of oxide with quartz and feldspar ground to about 100 mesh and the cans sealed. Larger containers for low-grade samples are desirable to increase the counting rate. However, such synthetic standards are not satisfactory for continued operation because the very fine BeO sifts through the rock powder and does not maintain a uniform distribution. Since a suitable binder without hydrogen or other element that might influence the neutron count has not yet been suggested, the best standard samples for continuous use are made from ground beryl and feldspar mixtures that have been sieved to a reasonably uniform size.

Care must be exercised in making comparative assays to ensure the maintenance of exactly the same geometry. The procedure followed in obtaining accurate assays with the portable instrument involves grinding and weighing and then compacting the sample into the can by pressing the material firmly down with the blade of a spatula. Any variation in bulk between samples is taken up by placing discs between the top of the sample and the lid of the container. The can is then inverted and the instrument lowered so the full weight of the instrument rests directly upon the bottom of the sample container. The operator can readily construct a simple guide to insure the uniform geometry. By following this procedure one should obtain reliable assays. Figure 5 shows the straight line curve obtained from standard samples made with known contents of beryllium oxide.

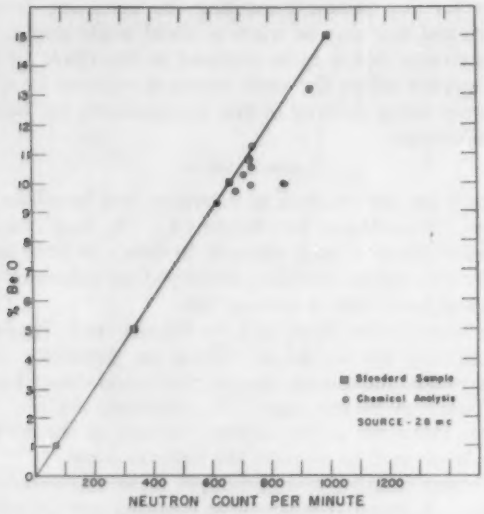

FIG. 5. Variation in the neutron count from beryllium-bearing samples is a straight line function of the beryllium content.

To obtain the true neutron count one must, of course, subtract the small background count from the total. Also, the discriminator setting must remain the same during readings of the background and sample counts. In counting random events, the standard deviation is the square root of the number of counts. The probable error is roughly two-thirds of the standard deviation. Thus, to attain an accuracy of about 1 percent, it is necessary to accumulate around 4,500 counts. However, for approximate assays, an accuracy of about 5 percent might be adequate for which a count of only 200 is required. With a 46-millicurie source, a 10 percent BeO sample of 80 grams weight will give a neutron count of 850 per minute or better, depending upon the efficiency of the phosphor. As the source becomes weaker, the time required will increase. The 80-gram sample of 1 percent BeO gave only 80 counts per minute with a source of about 38 millicuries, so for low material larger samples are desirable. Fig. 6 shows the effect of variation in size of sample. Curve A gives the neutron count for a series of 10 percent BeO samples of uniform diameter but increasing depth in 20-gram increments. No significant response was obtained beyond a depth of about 1.5 inches. Curve B was obtained from a test in which the depth of sample was uniform but the diameter progressively increased. With a depth of 1.55 inches, a 2 percent BeO sample attained its limiting value at a diameter of about 7 inches.

It is suggested, therefore, that a means of direct assaying is possible by setting the Berylometer on an outcrop and obtaining a neutron count from a volume of rock approximately the volume of a standard sample 1.5 inches

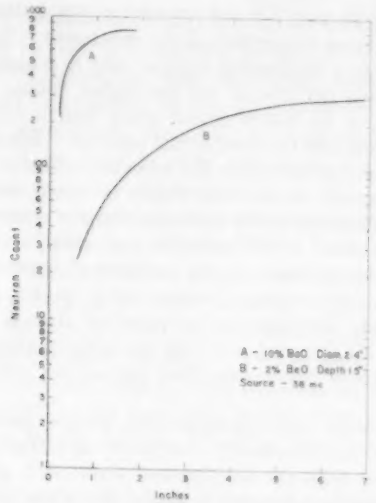

FIG. 6. Limiting range of beryllium activation as shown by the neutron count obtained from samples. A—with constant diameter but increasing thickness. B—constant thickness but with increasing diameter.

deep and 7 inches in diameter. Repeating this at uniformly spaced intervals, one could obtain a statistical average that would provide an evaluation for the area covered. Some allowance must be made for the irregularities of the rock surface because of the short range of the activation process. A preliminary test with a source at about 37 millicurie strength suggests that each reading be increased somewhat as follows:

relief $\frac{1}{16}$ inch—approximately 10 percent
$\frac{1}{8}$ inch—approximately 20 percent
$\frac{1}{4}$ inch—approximately 30 percent

Possibly some correction factors should be derived for the difference in density between the solid rock and the pulverized nature of the standard sample. However, the author has had no opportunity as yet to obtain this data nor to test this suggested direct method of evaluation of a beryllium-bearing deposit. But should it prove to be practical, there will undoubtedly be applications where it offers advantages over the conventional methods of cutting and preparing samples or the grain measurement method (7) of determining grade of a deposit. Most reliable results would, of course, be obtained where values are disseminated throughout the mass rather than concentrated in large isolated crystals.

A small portable impulse counter has been developed for use in the field with the Berylometer. It weighs only about 3 pounds, it is just 6.5 inches

long and is powered by two 7.5 volt transistor-type batteries. The cable to the counter uses the same connection as the earphones. The transistor circuit in the counter actuates a mechanical register that is reasonably accurate up to several hundred counts per minute but for higher counts it may be switched over to a scale of four by which device every fourth count received by the electronic circuit is fed into the mechanical counter. Should the scale of four be employed, one merely multiplies the recorded count by this factor and in this way the mechanical device can render a much more accurate count. Since, in practice, assays are made by comparing the neutron count of samples that are of the same order of BeO content, any small loss in count due to the relatively long resolving time of the mechanical counter applies to both. Figure 5 shows the distribution of assay values of ten chemically analyzed samples of high grade beryllium ore as obtained from a purchaser of beryl. These counts were all obtained with the portable mechanical counter on 80 gram samples and show reasonably close agreement with the four synthetic standards.

Commercial chemical and spectrographic assays for beryllium are relatively costly and all too frequently unreliable, and the advantages of being able to make analysis with the berylometer while on a prospect are obvious. A modified type of the Berylometer is available for use in a laboratory where heavier shielding permits the safe use of a stronger gamma source. The resulting higher counting rate then requires the use of a standard laboratory scaler. Also, the laboratory model provides for making analysis of aqueous solutions as well as solids.

EXPLORATION

The discovery of new sources of beryllium has, up until now, been largely dependent upon the recognition at sight of beryllium-bearing minerals. Apart from those occurrences of typically distinct yellowish green beryl crystals, visual identification is not easy. The most useful service the Berylometer can perform is to provide the prospector and exploration geologist with an instrument that can positively identify beryllium in any form. The discovery of beryllium in new and unsuspected relationships is to be expected. Also, in the re-examination of any known occurrence, there may be revealed an extension of boundaries or a distribution of associated deposits beyond the presently recognized boundaries. A few illustrations chosen at random may serve to illuminate these points.

Pegmatites.—The Harding Mine (8) in north-central New Mexico offers a good example of the occurrence of beryl in forms not easily recognized. This pegmatite had been mined for its content of lepidolite during the 1920's, and in 1942 for microlite. Not until 1942 was beryl recognized. It was mistaken for milky quartz, yet it occurred in masses up to eight feet thick. Some of it has a slight pinkish tint. This situation is not unique, however, for white beryl that is not easily distinguished from the surrounding feldspar and quartz is encountered in many pegmatites.

Large tonnages of disseminated beryl are known in the pegmatites of the tin-spodumene belt near King's Mountain, North Carolina (9). The only beryllium mineral yet recognized is beryl, making up about 0.4 percent of the rock, and this is evenly distributed as fine-grained crystals that may be recovered by milling at some future date. White beryl predominates and here also it is hard to recognize since its color and lustre are not very different from that of the associated quartz and feldspar.

Veins.—A substantial number of veins are reported to carry beryllium. The Boomer Mine, near Lake George in the Pike's Peak area, Colorado, was opened in 1956 in a vein that provided a considerable tonnage of direct shipping ore. Coarse beryl crystals carried most of the beryllium but there is also the mineral "bertrandite" (42% BeO), a colorless beryllium silicate derived from the hydrothermal alteration of beryl. This mineral is very difficult to recognize and its presence may render a vein richer in beryllium than a visual inspection would suggest. This vein also carries abundant topaz, fluorite, quartz and sericite and locally sulfides. Sulfides, however, are not a normal associate of beryllium.

Phenacite is a constituent of quartz veins and pegmatites of the Mount Antero region of Colorado (10), but the similarity between quartz and phenacite suggests that the latter mineral may be frequently overlooked. Both are hard vitreous minerals and each may occur in colorless hexagonal crystals that are indistinguishable except that quartz may be terminated by the six pyramid faces whereas the end of a phenacite crystal may rarely display only the three faces of a rhombohedron. Any high-temperature type of vein distinguished by the presence of fluorite, tin, tungsten, or molybdenum should be tested for the presence of beryllium.

An interesting beryllium vein is located about four miles north-east of Bagdad, Arizona, where a vertical albite dike about twelve inches wide traverses a massive biotite granite. A grayish green vein of beryl runs along one side of the felsite. This small vein, about two inches wide, possesses a crude radiating structure perpendicular to the contact. On the opposite side of the dike there is a fine-grained band of greenish material that resembles epidote, but the Berylometer readily showed that this material also is beryl.

Beryl-bearing veins have been found in a number of places in the southwestern United States and may be more common than generally recognized.

ACKNOWLEDGMENTS

The development of the Berylometer into a practical instrument for prospecting and laboratory analysis is not the accomplishment of any one person. The author gratefully acknowledges the contributions of his associates, K. I. Roulston, R. W. Pringle, and B. L. Funt; and to Nuclear Enterprises Ltd. of Winnipeg, especially A. M. Roulston, for assistance in experimental in-

strument construction; and to Dr. J. J. Norton for critically reading the manuscript.

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Author's Note: Since writing this paper, a method of bonding standard samples with sulphur has been adopted; and also a substantial increase in the neutron count has been achieved. For containing samples assaying in the 0.1 to 1.0 per cent BeO range, or lower, the 35 mm film can of 5 inch (2 pound) or 7 inch (3 pound) diameter is recommended.

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Economic Geology
Vol. 54, 1959, pp. 1115–1121

NOTE ON SOME CASSITERITE-BEARING PEGMATITES NEAR BRANDBERG, SOUTH WEST AFRICA

JOHN G. DENNIS

ABSTRACT

North of the Brandberg, South West Africa, cassiterite-bearing pegmatites are emplaced in Precambrian Lower Damara schists. Most of the pegmatites are in steeply northwest-dipping fractures parallel to layering in two small granite bodies associated with the pegmatites. Certain criteria suggest replacement origin for the pegmatites. Tin mineralization is in scattered greisenized zones and in quartz zones and veins.

THE cassiterite-bearing pegmatites here described are located north of the Brandberg (Figs. 1, 2), on both sides of the Ugab River. They differ in many important respects from other pegmatites in the neighborhood (1), (3), and the writer thinks that their mode of occurrence should be on record.

This note is based on field reconnaissance carried out in the early part of 1952 on behalf of the South West Africa Company. The writer is indebted to the South West Africa Company, and in particular to Mr. L. Ray, Mr. L. Bristowe and Dr. J. S. Brandt. Many helpful suggestions by Prof. C. H. Behre, Jr., and Dr. H. Martin are gratefully acknowledged.

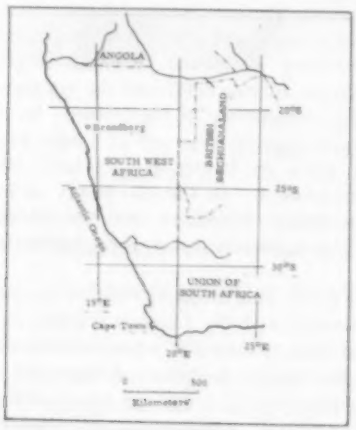


FIG. 1. Location.

GEOLOGIC SETTING

The country rock consists of a thick sequence of intensely deformed Precambrian (Lower Damara) schists in which are emplaced late phases of Salem granite (3, p. 19). Late syntectonic pegmatites in the Damara system have yielded age determinations ranging from 600 to 670 million years (4). Martin (6, p. 7) states that the Damara system is the geosynclinal equivalent of the Otavi system farther northeast.

These metamorphosed and deformed rocks are unconformably overlain by the normally flat-lying volcanics of the Kaoko series, which is probably of Stormberg (late Karroo) age. Near their contact with the Brandberg granite, the Kaoko beds dip inwards, toward the granite. The Kaoko series consists of sediments and volcanics. There is even a thin fluvio-glacial conglomerate at the base of the sediments on the northern side of Brandberg. This means that Dwyka and Stormberg beds are represented. The age range is Permian to lower Jurassic. (H. Martin, personal communication, 1958.) The Brandberg massif itself is a giant ring dike pluton of late Karroo or possibly post-Karroo age, intruded in the older rocks (2, 5) (Fig. 2).

LOWER DAMARA SCHISTS

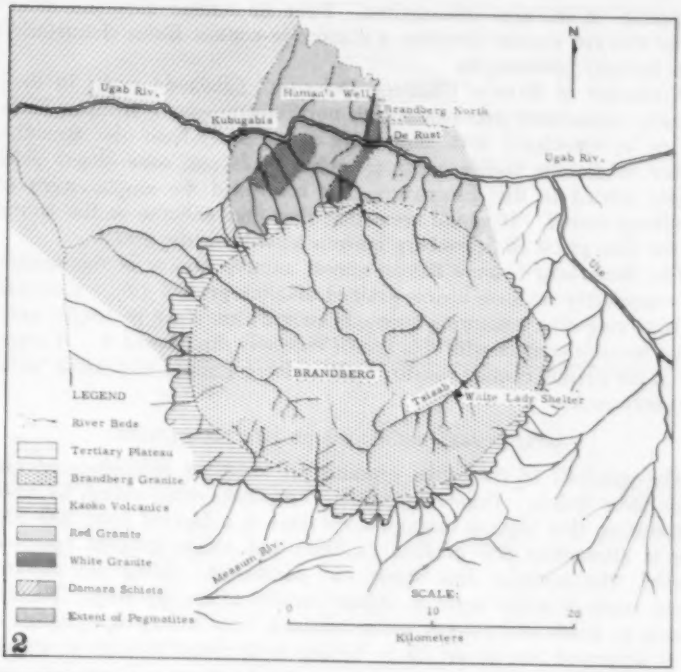
These schists are a thick sequence of pelitic and semipelitic rocks with interbedded marbles, amphibole schists and quartzites; they have remarkably uniform southeasterly dips. A number of isoclinal folds reveal a regional plunge of about 15° southwest. Lineations formed by the intersection of the dominant fracture system and bedding are usually parallel to the axis of folding. Schistosity is generally parallel to isoclinally folded bedding in this area, but transects the apeces of folds.

Igneous Rocks.—This heading includes three main granite bodies, numerous dike rocks, as well as the Kaoko lavas.

The White Granite is a non-porphyritic medium-grained somewhat aplitic granite with a cream-colored weathered surface. It occurs in two main bodies (Fig. 2). The cream surface color and the apparent lack of ferromagnesian minerals are due to weathering of the biotite. In the bottom of a few dry gorges the fresh granite may be observed as a light gray somewhat aplitic two-mica granite with white to faintly pink potash feldspars. Biotite is nevertheless a minor constituent. In the commonly seen weathered surface the biotite has been completely discolored, and the feldspars have turned a creamy yellow color. The cassiterite-bearing pegmatites are associated with this "White" granite.

The Red Granite (Fig. 2) is a muscovite-biotite granite with pink to red potash feldspars. Its contact with the Damara schists is nowhere exposed in the area here discussed, but it contains numerous disoriented xenoliths of schist. It has a traceable though indistinct contact with the White granite. There is no evidence, in this area, as to the relative age of these two granites.

Both composition and texture of the red granite are very variable, because of schist xenoliths in different stages of absorption. Reddening of the feld-



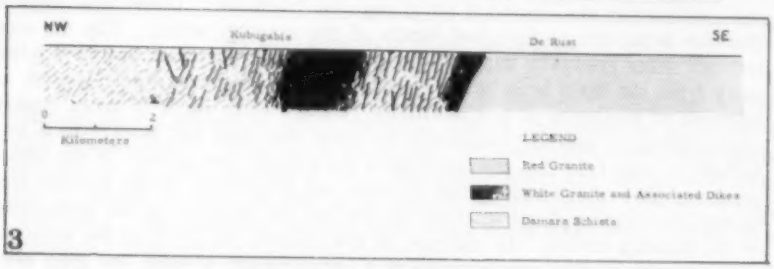


FIG. 2. Regional setting. Partly based on Cloos and Chudoba (1931).

FIG. 3. Cross-section parallel to Ugab River.

spars is commonly localized along joints and in pegmatites. Pegmatites in this granite occur as dikes and as schlieren. They are normally barren, and are notable for their low quartz content. Local concentrations of quartz are in many places accompanied by tourmaline. Beryl was found in two small pegmatites, and in each case this mineral was associated with much milky quartz. No other mineralization appears to be directly associated with the

red granite in the area investigated. Near its contact with the Brandberg granite this red granite develops a distinctive contact facies characterized by white feldspar phenocrysts.

A number of dikes of "Karroo Dolerites" (diabase) occur in the area, generally remarkably rectilinear with north-northeasterly strike. These appear to be associated with Stormberg volcanism. Near the Brandberg a number of diabase bodies occur as radial dikes and cone sheets evidently directly related to the disturbance that controlled the emplacement of the Brandberg massif. It would seem that ring dike collapse of the Brandberg was the final phase of Stormberg igneous activity in the area.

The Brandberg Granite has an almost circular outline at the surface and is a remarkably uniform coarse-grained alkaline granite (2). Essentially it is a large ring dike measuring approximately 25 km along its longer axis (5). Kaoko lavas in contact with this massif normally dip toward it. A transition zone at the granite contact consists of Brandberg granite with many inclusions of country rock.

STRUCTURAL RELATIONS OF THE PEGMATITES

The minerals of the white granites are oriented completely at random within these bodies. Pegmatites within the granite occur mainly as schlieren. Surrounding this random oriented core there is a layered zone 200–300 feet wide of alternating fine grained (aplitic) and coarse grained (pegmatitic) material; the layering dips about 70° northwest. Going out toward the schists, septa of schist begin to appear parallel to the layering. These septa increase in width and number going outward, until the aplo-pegmatitic material is separated into zoned 10 to 12-foot wide dikes, parallel in attitude to and emplaced in the dominant set of regional fractures. These facts suggest that the septa are undisturbed bands of the country schist. The distance between dikes gradually increases while their width decreases and, 2–3 miles away from the main body of white granite, they are very widely spaced, at intervals of hundreds of feet and more (though some occur in more closely spaced groups), and are commonly no more than two feet thick. It is important to note here that the layering in the granite, the attitude of the schist septa and that of the inner group of dikes are all parallel to one another and to the dominant regional fracture set, *not* to the bedding or the schistosity of the Damara schists. In contrast, in the classical tin fields of the adjacent regions, such as Uis, emplacement of a synkinematic granite, the gray porphyritic Salem granite and of many associated pegmatites, is mainly controlled by the bedding (3).

THE PEGMATITES

It would seem from the foregoing that the pegmatites were emplaced at the same time as the main granite body to which they are related, and that they are not late differentiates. In many cases they are cut and displaced by aplites. The pegmatites fall into three types, according to their occurrence in three belts: The inner belt, adjacent to the parent granite; the intermediate belt; and the outer belt, farthest from the parent granite.

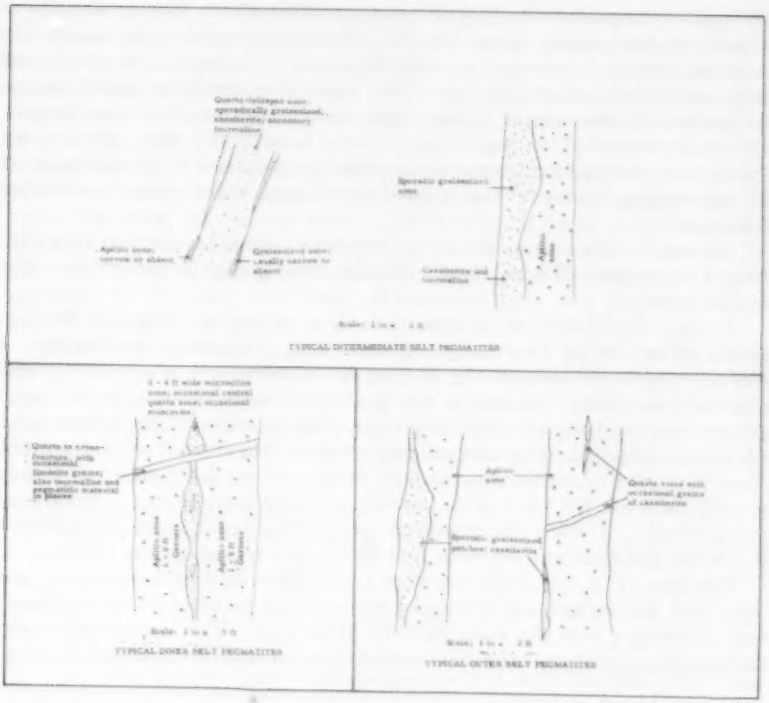


FIG. 4. Outcrops of typical pegmatites.

The inner belt pegmatites range from 12 to 20 feet in thickness. They actually consist mainly of aplitic material, with a few zones of large microcline phenocrysts. There are a few quartz cross-stringers, containing grains of limonite of uncertain derivation. The aplitic zones are dotted with small red to brown garnets, as well as a little accessory apatite, tourmaline, and muscovite. No cassiterite has ever been found in the inner belt. These dikes are almost invariably in west-dipping fractures.

The intermediate belt pegmatites are thinner than those of the inner belt, ranging from about 6 to 15 feet in thickness. They may contain feldspar phenocryst zones, but consist mainly of aplitic material. Many of these dikes have sporadic central quartz zones, especially those near the outer fringe of the intermediate belt. There are also quartz-filled cross-fractures. Unlike the inner belt, this belt has no garnets, but is characterized by maximum development of tourmaline and by sporadic greisenization in the pegmatites. In many places cassiterite occurs in these altered patches. Structural control here is similar to that of the inner belt, but pegmatites are also commonly found in east-dipping fractures. The outer belt pegmatitic dikes are thin;

their width ranges from an inch or less to about six feet. They consist almost entirely of fine-grained aplitic material with a few central quartz zones. In addition, quartz is common in cross-stringers. Tourmaline is absent, and large microcline phenocrysts are rare. Here any cassiterite mineralization is confined to the central quartz zones and to the quartz cross-stringers. Structural control of the pegmatites is rather loose in this belt. Most of the dikes are in the dominant west-dipping strike fractures and in the conjugate set of east-dipping fractures, but a number of them follow entirely unrelated fractures.

Throughout these areas the concentration of pegmatites decreases outward from the granite. Where dikes pinch out they grade, in many cases, into quartz veins.

Origin.—Field evidence appears to favor a replacement origin of the pegmatite dikes and of their parent granite body. Together, they occupy a sizable volume (cf. area on Fig. 2); yet the country rock is not in any way disturbed by them. Similarly, the gradual "disintegration" of the main granite body into dikes around its periphery, as described above, would favor a replacement origin by metasomatizing solutions that entered along fractures. Near the center of metasomatic activity these solutions followed many closely spaced fractures; the dikes grew laterally and soon merged into a continuous granite body. Toward the periphery of activity, fewer fractures admitted the fluids, less fluid was available, and the dikes were not able to coalesce.

Ramberg (7, p. 248–252) describes a mechanism of such replacement, and notes that the replacement pegmatite borders may be quite sharp, as indeed they normally are in the Kubugabis-De Rust area. This author also notes that very little additional material is required to accomplish the transformation.

TIN AND RELATED MINERALIZATION OF THE PEGMATITES

Cassiterite mineralization occurs in two distinct ways: 1. Much is associated with greisenization or sericitization, as in the intermediate belt. Cassiterite in this association normally occurs as small black grains (each about 2 mm, and generally less than 8 mm in diameter), not readily distinguishable visually from the ubiquitous tourmaline grains. 2. The remainder occurs as grains in quartz zones and stringers within pegmatites, as in the outer area. Here the cassiterite grains are normally reddish brown, rarely black. Their size ranges from about 2 to 20 mm.

Intermediate belt mineralization is associated with patches of pneumatolytic alteration (greisenization). All cassiterite grains are black, rarely more than 20 mm in diameter and generally much less. It seems possible that these patches are merely outcrops of elongated shoots.

This possibility can only be investigated by actual mining. Cassiterite mineralization is preferentially in apophyses of the pegmatite dikes, small satellite lenses and similar structures. It is almost invariably accompanied by tourmaline. This type of mineralization occurs at Kubugabis and at Brandberg North (Fig. 2).

The outer belt is mineralized in the Human's Well area only (Fig. 2). Cassiterite here occurs as reddish grains in central quartz zones and cross-cutting quartz stringers. Most pegmatites of this group carry a few scattered grains of cassiterite, but only a few carry concentrations of possible economic interest. Central quartz zones and cross-cutting quartz stringers were never observed together.

Cassiterite also occurs in quartz lenses, generally close to and evidently directly associated with mineralized pegmatites. In many places outer belt pegmatites grade into quartz veins. Chlorite may be an accessory mineral in this type of mineralization. Outer belt mineralization is more evenly distributed than intermediate belt mineralization. Its concentration in a given pegmatite is, however, very low. Mineralization is best in the dominant west-dipping fracture set.

A number of the dikes here described have been mined for cassiterite. However, alluvial concentrations related to the occurrences have proved far more rewarding, and even these are mostly marginal. With more promising prospects throughout the neighboring region, the marginal prospects of the Kubugabis-De Rust area are not likely to be exploited in the foreseeable future.

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Economic Geology
Vol. 54, 1959, pp. 1122–1125

SCIENTIFIC COMMUNICATIONS

THE APPLICATION OF Eh-pH DATA TO METASOMATIC DEPOSITS

JEROME F. MACHAMER

During a recent study of some metasomatic iron deposits, the writer concluded that the best explanation for the observed mineral assemblage and paragenetic sequence was provided by the application of data on the Eh-pH stability relations for the couples $S^{=}/SO_4^{=}$ and Fe^{++}/Fe^{+++}. The results of several recent studies of Eh-pH stability fields for iron minerals have been applied to sedimentary deposits, and similar studies on base metals have been applied to oxidizing sulfide deposits, but no previous application to metasomatic deposits is known. The writer feels that such applications offer a promising field for further research, and should provide a better understanding of those processes involved in the formation of metasomatic ore deposits.

The deposits studied are a group of magnetite deposits about six miles northwest of Ottawa, Ontario, which are currently being developed by Hull Iron Mines, Ltd., of Montreal, Quebec. They occur in Precambrian crystalline limestones associated with quartzites, schists, quartzo-feldspathic gneisses, and granitic rocks. The deposits themselves are magnetite lenses, carrying minor amounts of hematite, pyrite, pyrrhotite, and graphite, and trace amounts of chalcopyrite. The lenses occur in the flanks and nose of an overturned steeply plunging syncline, and parallel the plunge of the fold. The controlling structure is thought to be sheared zones parallel to the layering which developed during the waning stages of the deformation and metamorphism of the region. There is no readily apparent source for the mineralizing solutions.

The deposits can be divided into two groups. The most important are lenses composed primarily of magnetite that have formed by the replacement of relatively pure limestone. The second group consists of small lenses and disseminated patches of magnetite, accompanied by large amounts of sulfide and silicate minerals. These deposits occur in a zone of interbedded limestone and schist, and have developed through the replacement of narrow limestone layers, and calcite grains in the schist.

The paragenetic sequence is sulfides first, followed by magnetite and finally hematite, with quartz and calcite deposited irregularly throughout the sequence. This holds for the majority of the specimens studied, although there are local reversals. Relations between the sulfide minerals are such that no relative age sequence could be determined. Some of the hematite is due to relatively recent oxidation by circulating ground waters.

Certain assumptions may be made about the mineralizing solutions, and the environment in which the ore was deposited. Limestone is soluble in solutions whose pH is less than 7.8, under standard temperature and pressure conditions (3). This figure may vary somewhat with changing conditions, but the variation is probably not large. Since the limestone must be dissolved during the replacement, the pH of the solutions must have been below 7.8. The deposits are of Precambrian age, and were therefore probably formed at moderate to great depths, where the oxidation potential of ground waters and the environment in general would be very low. Under these conditions the iron in the mineralizing solutions would most likely be in the ferrous state, unless the solutions were moving downwards.

There are also certain facts regarding the solubility of iron compounds and the behavior of the carbonate ion which must be considered. The carbonate ions released during the solution of calcite will combine with hydrogen ions to form the bicarbonate ion, thus withdrawing hydrogen ions and increasing the pH of the solution. Both ferrous and ferric hydroxide will

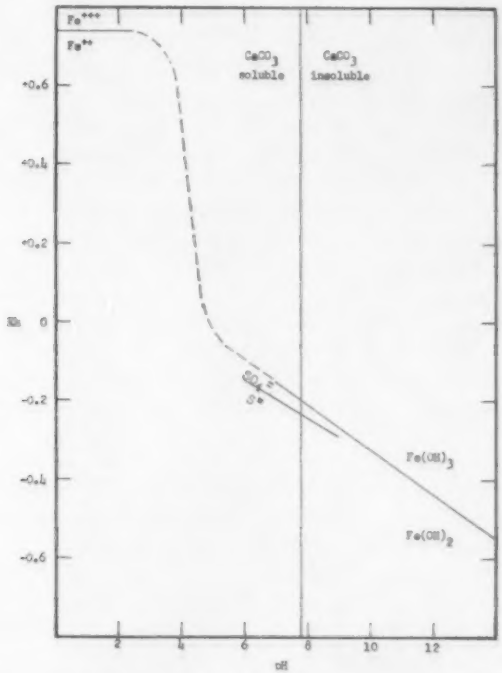

FIG. 1. Diagram showing the change in oxidation potential with pH for the couples $S^{=}/SO_4^{=}$ and Fe^{++}/Fe^{+++}, and the solubility of calcite. (Modified after Mason, 1958.)

precipitate from neutral and basic solutions when very small amounts of either ion are present (2). The mineral varieties of ferrous sulfide are insoluble in dilute acids, while ferrous sulfate is soluble under all conditions (2).

The variation of oxidation potential with pH for the couples $S^{=}/SO_4^{=}$ and Fe^{++}/Fe^{+++}, and the solubility of calcite, are shown in Figure 1. Given an oxidation potential in the neighborhood of -0.2, a solution of pH less than 7 carrying ferrous iron and small amounts of H_2S, which is becoming more alkaline, will deposit ferrous sulfide, ferrous hydroxide, calcium carbonate, and ferric hydroxide in that order. No ferrous sulfate would form, since it is soluble under any conditions; nor would any ferrous carbonate form, because it is soluble in solutions charged with CO_2 (2). Ferrous hydroxide, once precipitated, could undergo a process of self-oxidation according to the following reaction:

$$3Fe(OH)_2 = Fe_3O_4 + 2H_2O + 2H_2$$

resulting in the formation of magnetite (4); while ferric hydroxide could be dehydrated to form hematite.

The range of pH involved in this explanation is very small (i.e., from 6.5 to 8.5), and would be produced by the addition or subtraction of very small amounts of hydrogen ion (the reader is referred to acid-base titration curves in any text on quantitative analysis). Minor variations in oxidation potential are to be expected, and fluctuations in pH could easily be caused by the influx of fresh solutions. All the chemical reactions involved are known to take place under natural conditions, and the assumptions made are thought to be valid. The observed paragenetic sequence is exactly that which should occur under the conditions outlined, and the minor variations in Eh and pH could easily explain the local reversals in the paragenetic sequence. The greater amounts of sulfides in the one type of deposit are probably due to the lesser amount of limestone there, with the result that the solutions were not neutralized as rapidly, and sulfides were deposited for longer periods of time. Finally, this analysis is in agreement with data on the Eh-pH stability fields of iron minerals published in the March–April 1958 issue of this journal (1).

The experimental data on which this explanation is based were determined under standard temperature and pressure conditions. Theoretical values for dE/dT can be calculated, and indicate that all curves maintain their relative positions, but this is all that can be said at present about the effects of increased temperature and pressure. The effects of varying sulfur concentrations on the stability fields of the various iron minerals are large, but to date the calculations have been performed for only three concentrations (1). These are fields for further useful research.

Problems of this type cannot be solved definitely because the exact nature of the environment at the time of the formation of a deposit can never be known. Nevertheless it does appear necessary to consider the factors dis-

cussed in relation to what is known of the environments to arrive at the best possible hypotheses of origin.

DEPARTMENT OF GEOLOGICAL SCIENCES,
McGILL UNIVERSITY, MONTREAL, CANADA,
May 13, 1959

REFERENCES

1. Huber, N. K., 1958, The environmental control of sedimentary iron minerals: ECON. GEOL., v. 53, p. 123–140.
2. Lange, N. A., 1956, Handbook of Chemistry: 9th Ed., Handbook Publishers, Inc., Sandusky.
3. Mason, Brian, 1958, Principles of Geochemistry: 2nd Ed., John Wiley and Sons, New York.
4. Shand, S. J., 1947, The genesis of intrusive magnetite and related ores: ECON. GEOL., v. 42, p. 634.

Economic Geology
Vol. 54, 1959, pp. 1126–1127

DISCUSSIONS

COPPER URANIUM DEPOSITS IN PENNSYLVANIA

Sir: In the December 1958 issue of ECONOMIC GEOLOGY, Volume 53, pp. 1038 to 1042, J. F. McCauley describes the exsolution of chalcopyrite from bornite upon heating of specimens for a week at 180° C. The bornite specimens came from "Red Bed Copper Type Deposits" and originally showed a very faint exsolution texture.

The fact that considerable additional chalcopyrite exsolved from bornite after heating for two weeks at 180° C proves that the specimen was never exposed to such a high temperature for any geologically significant period of time in its original environment. Otherwise, it would be already exsolved. Any change in temperature in the deposit must have occurred over a period of years, and more likely thousands of years; this strongly suggests that the highest temperature to which the deposit was exposed was markedly lower than 180° C. It would be interesting to determine the lowest temperature at which any additional exsolution of chalcopyrite from bornite will occur in the laboratory, in an extremely short time geologically speaking. It will be the upper limit of the temperature of formation of the deposit.

The temperature of 400° C at which the exsolution texture disappears in bornite has been observed by other workers. It is suggested that this temperature corresponds more to that at which the homogenization takes place rapidly rather than to any definite point on the subsolidus curve for bornite-chalcopyrite.

Special care should be taken in polishing the section, as a rough treatment may be enough to cause some exsolution. No chemical changes are likely to affect the experiment because a loss of sulfur due to heating will not favor exsolution of chalcopyrite, and because bornite has a negligible compositional variation with respect to sulfur.

This writer thinks that J. F. McCauley's experiment is excellent proof of the low temperature at which the Red Bed Copper deposits in question were formed. A similar approach of studying disequilibrium mineral assemblages may perhaps be applicable to studies of other types of deposits.

This letter was written after a discussion with Dr. M. Sato, D. Emery, R. A. Navias and J. Phillips.

EDWIN H. GAUCHER

HARVARD UNIVERSITY,
ECONOMIC GEOLOGY DEPARTMENT,
CAMBRIDGE, MASS.,
March 21, 1959

THE WHITE PINE COPPER DEPOSIT

Sir: Mr. Reno Sales' discussion (This Journal) of the paper by Messrs. White and Wright on "The White Pine Copper Deposit" states the case for an epigenetic origin of this great copper deposit most convincingly.

A few additional facts disclosed by drilling add to the difficulty of accounting for the White Pine ore by syngenetic deposition. Among them are the following:

1. Mineralization near the White Pine Fault is not confined to one "thin stratigraphic horizon." In three sandstone beds in nearly 100 feet below the Parting Shale ore, excellent native copper and chalcocite mineralization with unusually high silver values extends for 1,000 to 2,000 feet or more northeast of the Fault. Elsewhere these deeper horizons are practically barren.

2. The ore mined in 1917 to 1920 in and close to the White Pine Fault zone is reported to have been very much richer than the normal White Pine bedded ore. There was also an unusually great proportion of native copper in the ore milled before 1920. No records are available as to whether the old workings showed vein mineralization or only drag ore in the Fault.

3. There are many seams, up to an inch or more wide, of steely chalcocite on steep fractures that cut the bedded White Pine ore.

If the syngenetic theory has any validity at White Pine, there has certainly been a great amount of solution, migration and redeposition of the copper subsequent to its original deposition. In fact the migration of the copper would have been so extensive that the term "syngenetic" would have little meaning if applied to the present orebodies.

In the White Pine orebody, as in the Rhodesian copper deposits, it is easy to pick flaws in either a syngenetic or an epigenetic theory of origin. Perhaps there may have been a complex history that did not fall into either category.

Mr. Sales' paper should lead to further interesting discussion of this old controversy.

IRA B. JORALEMON

SAN FRANCISCO, CALIF.,
May 18, 1959

ORE DEPOSITS AT SANTA BARBARA, MEXICO

Sir: I should like to add an item on mineralogy to those discussed by Mr. J. B. Scott (Vol. 53, p. 1017). While working in Santa Barbara in 1936, the writer collected two mineral specimens which attracted special attention. One was intimately associated with the dominant fluorite gangue on the lower level of the Alejandria mine. Optical and spectrographic tests proved it to be datolite, adding further to a unique mineralization. The second specimen was hedenbergite taken near the surface at one of the mines having footwall and hanging wall ore veins (not the Mina del Agua). Optical tests suggested that it was a nearly pure variety with perhaps a ratio of Fe: Mg as 9: 1. It occurred as a massive columnar mineral forming a distinct vein several inches wide associated with one of the ore-bearing veins.

GEORGE C. SELFRIDGE

ARLINGTON, VA.,
June 4, 1959

Economic Geology
Vol. 54, 1959, pp. 1128–1138

REVIEWS

TRANSLATIONS OF RECENT RUSSIAN LITERATURE

Méthodes d'Étude des Roches Sédimentaires. Edited by N. M. Strakhov. (Translation by J. P. de Saint-Aubin, A. Vatan, and others of *Metody Izucheniya Osadochnykh Porod*, 2 vols., Moscow, 1957.) In two volumes. Vol. i, pp. 542, pl. 43; vol. ii, pp. 535, pl. 8. Bureau de Recherches Géologiques, Géophysiques, et Minières, Paris, 1958. Quarto, off-set. Price, 16,000 francs (paper covers).

Grundzüge der Lithologie. By L. B. Ruchin. (Translation by A. Schüller of *Osnovy Litologii* by L. B. Rukhin, Moscow, 1953.) Pp. 806, figs. 304. Akademie Verlag, Berlin, 1958. Price, 56 DM.

The simultaneous appearance of French and German translations of two important Russian texts on the sedimentary rocks is symptomatic of the growing interest in sedimentation and sedimentary petrography to be found today in European laboratories. Strakhov's work, the original Russian edition of which has already been briefly noticed in Economic Geology (v. 53, p. 1058, 1958) represents the fulfilment of a program initiated in 1954 by the lithologists of the Academy of Sciences and of the Ministry of Geology, to prepare a comprehensive textbook for the use of those Russian students who aim at specializing in this field. It covers a wider range than current Western texts in that most of the well-established disciplines of field study and laboratory investigation are dealt with in one book; but as is perhaps natural in a work for students from the pens of no less than 40 authors, the depth of treatment is somewhat variable. Noteworthy omissions include the lack of any information on the radioactivity of the sedimentary rocks. The French translation, carried out with financial help from the Centre National de la Recherche Scientifique, has been prepared most expeditiously and is well produced, the plates and text-figures being superior in standard of reproduction to those of the Russian text; but unfortunately many obvious errors in the original stand uncorrected. To give but one example, figure 31 is printed sideways in both versions. In the bibliographies at the end of each chapter inherited misprints are frequent; and the use of strings of initial letters as abbreviated names for Russian institutions and periodicals is to be deprecated, for these will be generally unintelligible to Western readers. Such minor defects are however inseparable from rapid publication, and the B.R.G.G.M. (initials which nowadays need no elaboration!) is to be congratulated on its enterprise.

The German translation of Rukhin's lengthy monograph on the petrogenesis of sedimentary rocks has been financed by the East German Government and executed by an ideal editorial board of three—a translator and a stylistic editor under the command of an appropriately experienced scientist. The original work received a State prize when it was published in 1953; and to bridge the period since then the text has been fully revised and a good deal of new matter incorporated. It is complementary to the book by Strakhov in that it deals more with the results of researches than with the methods whereby they were executed. L. B.

Rukhin (Ruchin in German transliteration, Roukhine in French) has served the University of Leningrad as Aspirant, Assistant, Lecturer and (since 1945) Professor for 25 years, all occupied in studies of the genesis of sedimentary rocks and of their post-depositional changes; and except perhaps for a recent Russian symposium produced under his own editorship (ECONOMIC GEOLOGY, v. 54, p. 336, 1959) no single work makes quite such varied excursions throughout this large field as does the text under review. Of particular interest to the Western reader is the presentation of a fund of information about studies on the sedimentary rocks of the Soviet Union. A well-chosen bibliography of 161 items gives titles in Russian and in German translation; and the thoroughness of Professor Schüler's editing has resulted in the addition of good indexes, absent from the original edition.

Conditions de Formation des Gisements de Minérais. By P. M. TATARINOV. (Translation by H. Wierzbicki and J. Lougnon of *Usloviya Obrazovaniya Mestorozhdenii Poleznykh Iskopaemykh*, Moscow, 1955.) Pp. 215, figs. 77. Bureau de Recherches Géologiques, Géophysiques et Minières, Paris, 1959. Quarto, off-set. Price, 4,000 francs (paper covers).

This text on the origin and classification of ore deposits is based on a series of 40 lectures delivered to students and research workers at the Mining Institute of Leningrad. Whilst the author is too often at pains to demonstrate the "metaphysical" character of hypotheses originating from western scientists, most of his book (political issues apart) is thoroughly orthodox and seemingly devoid of major new conceptions of his own parentage. But in addition to great assiduity in compilation the work shows evidence of much deep thinking, and it may be read with profit and pleasure since it marries up a wide range of studies on Russian ore deposits to comparable investigations outside the Soviet Union. The translation reads well; but there are many mis-spellings due to double transliteration—Daubré for Daubrée, Clark for Clarke (repeatedly in the eponymous technical term), Scoope for Schoep, Trie-de-Terdonca for du Trieu de Terdonck, Komstock (Nevada) for Comstock, Seaward (Alaska) for Seward, and countless others. Despite these minor errors, the work is an interesting and acceptable addition to the first rank of textbook literature on economic geology.

The Geology of Uranium. (Translation of *Voprosy Geologii Urana*, Moscow, 1957.) 128 pp. Chapman & Hall, London; Consultants Bureau, New York. 1958. Quarto, Off-set. Price, £2. 8s.

An English translation of a Russian volume already reviewed (ECONOMIC GEOLOGY, v. 54, p. 149, 1959). The title is a misnomer, for the original work, a compilation of a dozen miscellaneous papers, was named "Contributions to the Geology of Uranium." The more important contributions have already appeared in English, in an expanded form, in the Proceedings of the United Nations Conference on Atomic Energy (Geneva, 1958).

C. F. DAVIDSON

UNIVERSITY OF ST. ANDREWS,
SCOTLAND,
June, 5, 1959

Geologia Applicata alla Ingegneria, 2nd Edition. By ARDITO DESIO. Pp. 1058; figs. 412. Ulrico Hoepli, Milan, Italy, 1959. Price, L.8500.

In the ten years since the first edition of this book geologic knowledge has grown greatly and so has the size of this volume—by over 200 pages. It is strictly a book of applied geology dealing with exploration, hydrology, applied geomorphology, geology of construction, and mining geology.

The first section deals with the constituents of the earth's crust, sedimentation, igneous activity, geologic mapping, geophysics of the earth, and geophysical prospecting. The second section delves thoroughly into applied hydrology. The third section on applied geomorphology takes up processes of weathering, river and sea erosion, sedimentation and glaciation, and forms the basic information for the geology of construction, which follows. This section covers all phases of engineering geology.

The last section on mining geology consists of 9 chapters. These deal with classification and forms of mineral deposits, magmatic, pneumatolytic and hydrothermal processes, and all other processes that give rise to mineral deposits. Different kinds of metallic and nonmetallic deposits are considered including coals and oil. Final chapters deal with methods of prospecting and radioactive minerals.

The book is well organized and illustrated and abundant references follow each chapter. It contains much information and should prove a good reference and textbook.

Vector Space and Its Application in Crystal-Structure Investigation. By MARTIN J. BUERGER. Pp. 347. John Wiley and Sons, New York, 1959. Price, $12.00.

This book by the noted author is intended for both academic and professional use by crystallographers, mineralogists, physicists, chemists, and metallurgists.

The chapter headings are: The Phase Problem of X-ray Crystallography; The Patterson Function; Some Early Intuitive Use of Patterson Maps; Further Theory of Patterson Functions; Patterson Functions for Special Cases; Patterson Projections of Symmetrical Crystals; Harker Sections and Implication Theory; Sets of Discrete Points and Their Vector Sets; Symmetry in Vector Space; Theory of Image-Seeking Functions; Superposition Functions; The Use of Image-Seeking Functions in Projections; The Use of Image-Seeking Functions in Three Dimensions; Substructures; and Retrospectus.

As may be seen from the titles of the chapters, this volume is a systematic exposition of vector space and its applications in crystallography. The author has assumed a general knowledge of crystal-structure analysis and develops the possibility of a solution of the phase problem of x-ray crystallography for certain symmetrical crystals of limited complexity.

This third book of Professor Buerger's marks an outstanding advance in this field.

The Canadian Northwest: Its Potentialities. A Symposium, edited by FRANK H. UNDERHILL. Pp. 104. Univ. of Toronto Press, Toronto, Ontario, 1959. Price, $4.00.

This volume is the result of a symposium presented to the Royal Society of Canada in 1958. It consists of seven papers as follows: Introduction, by Abbé d'Eschambault; Engineering Assessment, by Robert F. Legget; Assessment by a Geographer, by W. C. Wonders; Minerals and Fuels, by A. H. Lang and R. J. W.

Douglas; Biological Potentialities, by D. S. Rawson; The Resources Future, by D. B. Turner; A Prelude to Self Government: The Northwest Territories 1950–1939, by Morris Zaslow.

These papers depict the great economic expansion of this part of Canada since World War II. The spectacular developments have been uranium, nickel, gold, oil and gas wells, water power developments to make aluminum, pipelines, lumber, and fisheries. Silver, lead, zinc, copper, and asbestos add additional value. The total annual mineral production alone is about 92 million dollars.

The seven articles give a broad picture of the resources and particularly of the potentials of this great region, which is about one-fifth of the area of Canada.

Environmental Conservation. By RAYMOND F. DASMANN. Pp. 305; figs. 153. John Wiley & Sons, New York, 1959. Price, $6.50.

This book is intended as an elementary text for a one semester course in conservation and is written from a biological standpoint. It is an ecological approach to the conservation of natural resources with emphasis on the land and waters of the earth. Land use and population problems are given a historical perspective.

The twelve chapters deal with the nature of natural resources, biotic regions, man's record on the earth, soil conservation, forests, livestock, animal life, fisheries, population, conservation of environments, and the outlook. References are given after each chapter.

The author is Associate Professor and Head of Game Management, Division of Natural Resources, at Humboldt State College, and signs himself as M.A., Ph.D. The book has many interesting pictures.

Mineralogy, An Introduction to the Study of Minerals and Crystals, 5th Edit. By E. H. KRAUS, W. F. HUNT, and L. S. RAMSDELL. Pp. 686; figs. 736. McGraw-Hill Book Co., New York, Toronto, London, 1959. Price, $9.00.

The preceding four editions since 1920 have made this book well known to all mineralogists and geologists. This last edition is a few pages longer than its predecessor, but contains considerable new material, particularly on Chemical Mineralogy and Crystal Chemistry, and Formation and Occurrence of Rocks and Minerals. There is also some revision of the chemical formulas of certain minerals resulting from newer x-ray studies.

As before, the book deals with crystallography, crystal systems, physical and optical properties, crystal structure, descriptive mineralogy, classification of minerals, and glossary. Tables on classification of the classes of symmetry and determination of minerals occupy 182 pages.

The new edition will continue to be a useful and authoritative book on mineralogy and crystallography.

BOOKS RECEIVED

JOHN E. COTTON AND CYRUS W. FIELD

Automation, Cybernetics and Society. F. H. GEORGE. Pp. 283; figs. 23. Philosophical Library, New York, 1959. Price, $12.00. *A discussion of automation, cybernetics, psychology, and philosophy in relation to society in the age of automation; a clarification for the scientist, the executive and the layman.*

Dolerite: A Symposium—Held in the Geology Department of the University of Tasmania in July 1957. S. WARREN CAREY, CONVENER. Pp. 274; pls. 5;

figs. 67; tbls. 18. University of Tasmania, Hobart, 1958. *A comprehensive symposium initiated by Professor S. W. Carey. Participants discussed in relation to dolerite the problems associated with intrusion, differentiation, structure, relation to country rocks, weathering, soil formation, and other aspects.*

Geologija, Razprave in Poročila (Geological Transactions and Reports). Geological Survey in Ljubljana, Vol. 4, 1958 (1959). *Sixteen articles on Yugoslavia geology; eight are followed by English translations, two by German, and one by French. Included are the geology of the Idrija mercury mine, the Gornja Lipa copper deposit, and the Mezica deposit. Geologic maps have English titles.*

The Mining Journal, Annual Review 1959. Pp. 347. The Mining Journal Ltd., London, 1959. Price, 21/–. *Review of metals and minerals, technical progress, world's mining fields in 1958, progress of mining companies, professional directory, buyers guide, and index.*

Statistical Summary of the Mineral Industry 1952–1957. Pp. 357. Overseas Geological Surveys, Mineral Resources Division, Her Majesty's Stationery Office, London, 1959. Price, £1, 7s. 6d. *Production, exports, and imports of 70 metals and minerals, by British countries and foreign countries; list of statistical publications.*

Resumes des Communications du Colloque International Organisé par L'Université de Liège. Pp. 16. Liege, 1959. *A collection of 11 articles concerning various geologic problems encountered in dam construction.*

Canada Department of Mines and Technical Surveys Annual Report Calendar Year 1957. Pp. 142. Ottawa, 1959. Price, 50 cents.

The Geology of the Xeros-Troodos Area. With An Account of the Mineral Resources. R. A. M. Wilson. F. T. Ingham. Pp. 184; pls. 10; figs. 20; tbls. 4. Price, £1. Geological Survey Department Cyprus Memoir 1. *An excellent, well-illustrated geologic report of the xeros-troodos are in west-central Cyprus. The stratigraphy, petrology, and economic geology are treated extensively. Two geologic maps, scale 1:31,680, are included in the pocket.*

Die Gattung Macrodentina und Einige Andere Ostracoden-Arten aus dem Oberen Jura von NW-Deutschland, England und Frankreich. Heinz Malz. Pp. 67; pls. 11; figs. 4; tbls. 3. Abhandlungen der Senckenbergischen Naturforschenden Gesellschaft, Frankfurt am Main, 1958. *A well-illustrated report on Macrodentina and other ostrocods from Upper Jurassic strata of Europe.*

The Mineral Wealth of Madhya Pradesh, Vol. II, No. 1. Pp. 34. India Dept. of Geology and Mining, Raipur, 1958. *Eight articles. Two deal with coal fields; one each, with petroleum, mineral production, mineral economics, and future investigations. Contains symbolic mineral industrial map of Madhya Pradesh.*

Bibliography of Geology, Palaeontology, Industrial Minerals, and Fuels in the Post-Cambrian Regions of Manitoba 1950 to 1957. B. A. Mills. Pp. 32. Dept. of Mines and Natural Resources Publ. 57-4, Winnipeg, Canada, 1959.

The Geology of Part of the Mzimba and Rumpi Districts (Luwewe and Upper South Rukuru Valleys). W. H. Reeve. Pp. 22; geological map, scale 4 miles:1 inch. Geological Survey of Nyasaland Rept. 2, Zomba, 1958. *Economic mineral possibilities of this area are not encouraging.*

Anthracologic Analysis—A Guide to the Applied Petrology of Ohio Coals. Gilbert H. Cady. Pp. 83; figs. 18; tbls. 6. Ohio Geological Survey Information Circ. 22, Columbus, 1958. *The general purpose of this study has been to describe*

and evaluate various procedures and techniques available for use in the petrographic description and analysis of coal beds.

Geological Map of the Province of Ontario. Scale, 1 inch: 20 miles. Size 56 × 40 inches. In color. Map No. 1958B. Ontario Dept. of Mines, Toronto, 1959.

Prospecting and Exploration in South Sinai 1953–1954. SAYED ABDEL NASER and BAHA EL-DIN CHUKRI. Pp. 36; pls. 15; geologic map, scale 1: 100,000. Dept. of Mines and Quarries, Sinai. *The copper deposits and small coal deposits merit further study.*

The Geology of a Portion of the Inyanga District. R. TYNDALE-BISCOE. Pp. 11; map, scale 1: 250,000. Southern Rhodesia Geological Survey Short Report 37, Salisbury. *A brief discussion of rock types and regional physiography.*

Report of the Geological Department for the Year 1957. Pp. 16; tbls. 3. Price, 2 shillings. Sierra Leone, 1959. *Report of geologic investigations in Sierra Leone for 1957.*

Geology of the Beaconsfield District, Including the Anderson's Creek Ultrabasic Complex. DAVID H. GREEN. Pp. 25; figs. 5; colored map. University of Tasmania Dept. of Geology Publication 65, Hobart, 1959. *Stratigraphy, petrology, and structural geology of the Beaconsfield District, Tasmania.*

Les Terrains Precambriens du Togo et Leur Extension vers le Nord-Est. P. AICARD. Pp. 221; pls. 31; tbls. 15. Direction des Mines et de la Géologie, Republique du Togo, Dakar, 1957. *An excellent well-illustrated geologic report on the Precambrian rocks of the Togo region. The petrology of the meta-sediments and intrusives are discussed extensively. Mineralization in the area is sparse though small non-commercial deposits of lead, chrome, gold, rutile, and serpentine were noted.*

Annual Report of the Geological Survey Department for the Year Ended 31st December, 1958. Pp. 18. Price, Shs. 2. Uganda Protectorate, Entebbe, 1959.

Geological Survey of India—Delhi, 1953, 1955.

Records of the Geological Survey of India Vol. 79, Pt. 1, 1953. Pp. 385. Price, Rs. 8 or 13 sh. *M. S. Krishnan authors the General Report of the Survey for the years 1940, 1941, and 1942.*

Records of the Geological Survey of India, Vol. 79, Pt. 2, 1955. Pp. 387–872. Price, Rs. 9-4 or 14 sh. 6d. *M. S. Krishnan authors the General Report of the Survey for the years 1943, 1944, 1945, and 1946.*

Geological Survey of Kansas—Lawrence, 1959.

Bull. 134, Pt. 2. Cement Raw Materials in Kansas. RUSSELL T. RUNNELS. Pp. 105–124; figs. 5; tbls. 3. *All of the eastern one-third and much of central Kansas has abundant rock suitable for the manufacture of portland cement.*

Bull. 137. Symposium on Geophysics in Kansas. Edited by WILLIAM W. HAMBLETON. Pp. 375; pls. 2; figs. 159; tbls. 4. *This collection of 25 papers deals with all phases of geophysics and geophysical exploration in the state.*

Bull. 139. Geology and Ground-Water Resources of Cloud County, Kansas. C. K. BAYNE and K. L. WALTERS. With a section on **Ceramic Materials,** by NORMAN PLUMMER. Pp. 144; pls. 3; figs. 21; tbls. 16. *The unconsolidated sand and gravel deposits of Pleistocene age form the principal aquifers.*

Institutes of Mineralogy, Paleontology, and Quaternary Geology, University of Lund, Sweden, 1958. (Reprinted from Kungl. Fysiografiska Sallskapets i Lund Forhandlinger.)

Publ. 46. Origin of the Manganese Ore Deposit of Bolet, Southern Sweden. PONTUS LJUNGGREN. Pp. 95–107; figs. 2. *Quadrivalent manganese oxides are considered to have constituted the primary manganese compounds. These were changed to manganites in brecciated zones under a reducing environment. In English.*

Publ. 47. The Black Beach Sands of Iztapa on the Pacific Coast of Guatemala. PONTUS LJUNGGREN. Pp. 109–119; fig. 1; tbls. 4. *These sands originate from the decomposition of andesitic and basaltic eruption products. In English.*

Publ. 48. A Mineralogical Examination of Some Soil Samples from Southern and Central Honduras. PONTUS LJUNGGREN. Pp. 125–131; figs. 2. *Highland soils are rich in kaolinite and montmorillonite, whereas hydrous alumina minerals are abundant in lowland soils. In English.*

Publ. 49. Mineralogical Examination of Black Beach Sands from "Lago de Izabel," Eastern Guatemala. PONTUS LJUNGGREN. Pp. 133–139; fig. 1; tbls. 5. *Samples from one locality are 82.6% ilmenite. Possible enrichment of chromite in sands of this region is discussed. In English.*

Western Australia Geological Survey—Perth, 1958.

Bull. 110. The Geology of the Phillips River Goldfield, W. A. JOHN SOFOULIS. Misc. reports by J. Sofoulis and A. J. Noldart. Pp. 240; pls. 1 in bulletin and 16 in separate accompanying atlas; figs. 17; tbls. 9. *This bulletin deals with the physiography, general, structural, and economic geology of some 4,500 square miles containing rocks of three principal geological ages—Archaean, Proterozoic and Tertiary.*

Report of the Geological Survey Branch for the Year 1956. Extract from the Report of the Department of Mines. Pp. 7. *Annual progress report.*

U. S. Geological Survey—Washington, D. C., 1959.

Bull. 1019-N. Selected Bibliography of Andalusite, Kyanite, Sillimanite, Dumortierite Topaz, and Pyrophyllite in the United States. AGNES B. GRAMETBAUR. Pp. 973–1046; pl. 1. Price, 45 cents. *Contains references, to December 31, 1958, on geology, mineral synthesis, geographic occurrence, and technology and uses.*

Bull. 1028-J. Geologic Reconnaissance of Gareloi Island Aleutian Islands, Alaska. ROBERT R. COATS. Pp. 249–256; pls. 3. *Volcanic activity has occurred in two periods separated by a long period of volcanic quiescence and erosion.*

Bull. 1028-K. Geology of Segula, Davidof and Khvostof Islands, Alaska. W. H. NELSON. Pp. 257–266; pls. 3; fig. 1. *These volcanic islands rise from a submarine platform about 350 feet below sea level.*

Bull. 1046-K. Results of Geologic Exploration by Core Drilling, 1953, Land-Pebble Phosphate District, Florida. J. B. CATHCART and L. J. MCGREEVY. Pp. 221–298; pls. 19; fig. 1. *The phosphate deposits of this district are partly residual, partly marine reworked, and partly phosphatized clay.*

Bull. 1072-E. Areal Geology of the Placerville Quadrangle San Miguel County, Colorado. A. L. BUSH, C. S. BROMFIELD, and C. T. PIERSON. Pp. 299–384; pls. 5; figs. 4. *This quadrangle is on the northeast boundary of the*

Colorado Plateau's physiographic province adjacent to the San Juan Mountains. The geology reflects the geologic events and processes of the two provinces.

Bull. 1081-A. Graphic-Locator Method in Geologic Mapping. D. J. VARNES, T. L. FINNELL, and E. V. POST. Pp. 10; pl. 1; figs. 4. Price, 15 cents. *A device used with a topographic map and a sighting instrument to determine the point at which a line of sight intersects the ground surface.*

Bull. 1086-E. Index to Geophysical Abstracts 172–175, 1958. DOROTHY B. VITALIANO AND OTHERS. Pp. 467–551. Price, 35 cents.

Bull. 1106-A. Geophysical Abstracts 176 January–March, 1959. D. B. VITALIANO, S. T. VESSELOWSKY, AND OTHERS. Pp. 128. Price, 35 cents.

Bull. 1028-I. Geology of the Delarof and Westernmost Andreanof Islands Aleutian Islands, Alaska. G. C. FRASER and H. F. BARNETT. Pp. 211–248; pls. 6; tbls. 2; figs. 4. *Geology and geomorphology of some volcanic islands of the Aleutian chain. Four geologic maps.*

Bull. 1045-E. Core Logs from Searles Lake, San Bernardino County, California. DAVID V. HAINES. Pp. 139–317; pls. 6; figs. 2. Price, $2.00. *A preliminary report of the mineralogy, shape, and thickness of this saline deposit based upon 41 cored and logged drill holes on Searles Lake.*

Bull. 1052-H. Dielectric Constant and Electrical Resistivity of Natural-State Cores. G. V. KELLER and P. H. LICASTRO. Pp. 257–285; tbls. 2; figs. 21. Price, 20 cents. *Results of a program to determine the physical properties of rocks in and near uranium-mineralized zones. The water content of cores appears to be the controlling factor. With high water content, low resistivity and high dielectric constants were encountered.*

Bull. 1073. Quaternary Geology of the Smoke Creek-Medicine Lake-Grenora Area, Montana and North Dakota. IRVING J. WITKIND. Pp. 80; pls. 10; figs. 19. Price, $1.75. *Stratigraphy and structure of Quaternary sediments of Montana and North Dakota. The elongate occurrence of sodium sulfate deposits in basin-like depressions is attributed to ice-marginal channels.*

Prof. Paper 260-W. Lower Eocene Phosphatized *Globigerina* Ooze from Sylvania Guyot. E. L. HAMILTON and R. W. REX. Pp. 785–798; pls. 5; fig. 1. *A study of the mode of occurrence, mineralogy, and paleontology of fossil **Globigerina** oozes.*

Prof. Paper 280-K. Geology of Saipan Mariana Islands. Pt. 4. Submarine Topography and Shoal-Water Ecology. PRESTON E. CLOUD, JR. Pp. 361–446; pls. 21; figs. 8; tbls. 6. *A study of the submarine topography and of the sediments, biotas, and morphology of the reef complex adjacent to Saipan.*

Prof. Paper 294-J. Conodonts from the Chappel Limestone of Texas. WILBERT H. HASS. Pp. 365–399; pls. 5; fig. 1; tbl. 1; chart 1. *Division of the formation into three faunal zones, description of species, and presentation of utilitarian classification of disjunct conodonts.*

Prof. Paper 302-A. Phosphate Deposits in Northern Alaska. Exploration of Naval Petroleum Reserve No. 4 and Adjacent Areas, Northern Alaska, 1944–53. Pt. 4, Regional Studies. W. W. PATTON, JR., and J. J. MATZKO. Pp. 17; pls. 6; figs. 3. Price, $1.00. *The uraniferous phosphate rock is similar in mineralogy, phosphate, uranium, and minor element content to phosphates from the Phosphoria formation.*

Prof. Paper 302-B. Vegetation of the Arctic Slope of Alaska. Exploration of Naval Petroleum Reserve No. 4 and Adjacent Areas, Northern Alaska, 1944–53. Pt. 2, Regional Studies. LLOYD A. SPETZMAN. Pp. 19–58; pls. 6; figs. 5; tbls. 3. Price, 55 cents. *Six major plant communities comprising the tundra of these areas and their relation to various rock types are discussed.*

Prof. Paper 305-I. Core Test, Sentinel Hill Area, and Test Well Fish Creek Area, Alaska. Exploration of Naval Petroleum Reserve No. 4 and Adjacent Areas, Northern Alaska, 1944–53. Pt. 5, Subsurface Geology and Engineering Data. F. M. ROBINSON and F. R. COLLINS. Pp. 485–521; pls. 4; figs. 5. Price, $1.00. *Description of lithology and results of two drill holes from the Naval Petroleum Reserve No. 4 and adjacent areas. A small amount of heavy black oil was recovered from the test well at Fish Creek.*

Prof. Paper 307. Geology of the Pierre Area South Dakota. DWIGHT R. CRANDELL. Pp. 83; pls. 3; figs. 33. *The Missouri River bisects the area; the region to the northeast has glacial deposits overlying Pierre shale; and the region to the southwest consists of Pierre shale.*

Prof. Paper 314-G. Succession and Speciation of the Pelecypod *Aucella* RALPH W. IMLAY. Pp. 155–169; pls. 4; fig. 1; tbl. 1. *The author recommends that species of Aucella be defined with due allowance for biological and environmental factors thereby rendering them applicable for mapping purposes by field geologists.*

Prof. Paper 316-A. Regional Geophysical Investigations of the Uravan Area, Colorado. H. R. JOESTING and P. E. BYERLY. Pp. 17; pls. 3; figs. 5. Price, $1.25. *Magnetic and gravity trends in the Uravan Area are generally parallel to the northwestward-trending regional structural features.*

Prof. Paper 319. Geology and Ore Deposits of the Chicago Creek Area Clear Creek County, Colorado. J. E. HARRISON and J. D. WELLS. Pp. 92; pls. 13; figs. 38; tbls. 15. *Includes a description of the geologic formations; discussions of the structural history, abnormal radioactivity of veins and rock, localization of ore bodies, and descriptions of individual mines.*

Prof. Paper 321. Cenozoic Echinoids of Eastern United States. C. WYTHE COOKE. Pp. 106; pls. 43. *Describes and illustrates fossil and Recent sea urchins.*

Prof. Paper 327. Geology and Mineral Resources of Paraguay—A Reconnaissance. EDWIN B. ECKEL. **Igneous and Metamorphic Rocks.** CHARLES MILTON and E. B. ECKEL. **Soils.** P. T. SULSONA. Pp. 110; pls. 3; figs. 58; tbls. 6. *Results of a 6-month reconnaissance survey of the geology and mineral resources of Paraguay included with a compilation and interpretation of existing published and unpublished information. Geologic map of Paraguay, scale 1:1,000,000.*

Prof. Paper 334-A. Tables for the Calculation of Lead Isotope Ages. L. R. STIEFF, T. W. STERN, SEIKI OSHIRO, and F. E. SENFTLE. Pp. 40; figs. 2; tbls. 4. Price, 35 cents. *These tables use the atomic ratios of Pb^{206}/U^{238}, Pb^{207}/U^{235}, Pb^{207}/Pb^{206}, and Pb^{208}/Th^{232}.*

Water-Supply Paper 1260-F. Summary of Floods in the United States During 1952. L. P. LEOPOLD under direction of J. V. B. WELLS. Pp. 687–713; tbl. 1; figs. 2. Price, 20 cents. *In 1952 extensive flooding occurred in the northern basins of the Missouri, upper Mississippi, and Red Rivers. The states of Texas, Utah, Nevada, and California were the localities of other large floods.*

Water-Supply Paper 1320-C. Floods of April–June 1953 in Louisiana and Adjacent States. C. G. PAULSEN under direction of J. V. B. WELLS. Pp. 155–320; pls. 4; figs. 24; tbls. 4. *High soil moisture content and streamflow resulting from rains in April set the stage for record floods in May.*

Water-Supply Paper 1460-F. Geologic Reconnaissance and Test-Well Drilling Camp Irwin, California. FRED KUNKEL and F. S. RILEY. Pp. 233–271; pl. 1; fig. 1. *Results of this survey indicate that unconsolidated sediments of the region have the greatest potential for ground water storage, transmittance, and yield.*

Water-Supply Paper 1460-G. Ground-Water Resources of the Lower Niobrara River and Ponca Creek Basins, Nebraska and South Dakota. T. G. NEWPORT. **Chemical Quality of the Water.** R. A. KRIEGER. Pp. 273–323; pls. 3; figs. 7; tbls. 5. *A thorough report on the ground water resources of several basins in Nebraska and South Dakota complete with annotated bibliography of previous publications of the area.*

Water-Supply Paper 1465. Quality of Surface Waters for Irrigation Western United States 1955. Pp. 189; pl. 1. *Empirical equations are used in evaluating the salinity, sodium, boron, and bicarbonate ion hazards following the 1954 classification of the U. S. Salinity Laboratory Staff.*

Water-Supply Paper 1467. Ground-Water Appraisal of Santa Ynez River Basin Santa Barbara County, California, 1945–52. H. D. WILSON, JR. Pp. 119; pls. 8; figs. 20; tbls. 9. *Accurate estimates of perennial yield must await further data. During the 1945–52 period ground-water levels declined.*

Water Supply Paper 1468. Geology and Ground-Water Resources of Clay County, Nebraska. C. F. KEECH and V. H. DRESSEN. **Chemical Quality of the Water.** F. H. RAINWATER. Pp. 157; pls. 4; figs. 17; tbls. 12. Price, $1.50. *Tertiary continental deposits and Quaternary sands and gravels provide sufficient ground water reserves for greater withdrawals than at present.*

Water-Supply Paper 1470. Geology and Ground-Water Features of the Eureka Area Humboldt County, California. R. E. EVENSON. Pp. 80; pls. 2; figs. 15; tbls. 11. *Most of the ground water occurs in deposits ranging in age from Pliocene to Recent.*

Water-Supply Paper 1472. Hydrologic Budget of the Beaverdam Creek Basin Maryland. W. C. RASMUSSEN and G. E. ANDREASEN. Pp. 106; pls. 10; tbls. 10; figs. 19. *Results of a two-year study of the hydrologic budget from a selected basin on the Atlantic Coastal Plain. The ground water potential might be increased through utilization of unused streamflow and the removal of nonbeneficial plants.*

Water-Supply Paper 1473. Study and Interpretation of the Chemical Characteristics of Natural Water. JOHN D. HEM. Pp. 269; pls. 2; figs. 40; tbls. 26. *A comprehensive study of the chemical properties and constituents of natural waters.*

Water-Supply Paper 1474. Geology and Ground-Water Resources of the Big Blue River Basin Above Crete, Nebraska. C. R. JOHNSON and C. F. KEECH. **Chemical Quality of the Water.** ROBERT BRENNAN. Pp. 94; pls. 2; figs. 10; tbls. 5. Price, 75 cents. *Sand and gravel of Pleistocene age yield larger quantities of ground water of the calcium bicarbonate type.*

Water-Supply paper 1476. Investigations of Sediment Transportation Middle Loup River at Dunning, Nebraska. D. W. HUBBELL and D. Q. MATEJKA.

Pp. 123; pls. 13; figs. 38; tbls. 9. *Sediment discharges have been computed with several different formulas and the computed loads have been compared with data from an artificial turbulence flume.*

Water-Supply Paper 1496-A. A Survey of Analytical Methods for the Determination of Strontium in Natural Water. C. ALBERT HORR. Pp. 18. Price, 15 cents. *Satisfactory methods depending upon the conditions include gravimetrical, volumetrical, and emission spectrochemical methods, flame photometry, X-ray spectroscopy, column and paper chromatographic methods, and radiochemical methods.*

Economic Geology
Vol. 54, 1959, pp. 1139–1147

SOCIETY OF ECONOMIC GEOLOGISTS

A SPECIAL MEETING of the Society of Economic Geologists will be held in the William Penn Hotel, Pittsburgh, Pa., *on Sunday, November 1, 1959.* The purpose: *To hold a symposium on "The role of stable isotope research in the field of ore deposits."*

The meeting will convene at *2 P.M.*

The program will include the reading and discussion of a number of papers specially prepared to review results that are being attained from isotopic research and their potential value and application in the study and discovery of ore deposits.

The afternoon session will be followed by a social hour and Society dinner, after which the technical discussions will be resumed.

The regular fall meeting of the Society of Economic Geologists will be held in Pittsburgh, Pa., November 2–4, in conjunction with the annual meetings of the Geological Society of America and associated societies. Headquarters for the meeting will be in the William Penn Hotel.

PROCEEDINGS OF THE SOCIETY OF ECONOMIC GEOLOGISTS FOR THE SOCIETY YEAR 1958

At a meeting held in San Francisco on February 19, 1959, the Council voted to print the Annual Proceedings of the Society in Economic Geology. With this issue then, the Council returns to its original practice of publishing the Proceedings annually rather than holding them for issue in groups of 3 or 4 as has been the custom over the past three decades.

Report of the President

The Society year 1958 extended from April 1, 1958 to March 31, 1959. In the opinion of the President, it was a successful year and was marked by real progress in fulfilling the purposes of the Society. Much of the credit for improvement in affairs of the Society resulted from actions set in motion by Francis Cameron during his term as President in 1956.

The professional nature of the Society has been re-emphasized by elimination of credit for undergraduate work in computing the eight years of experience necessary for membership. The Society has grown slowly in recent years, but informal efforts to bring in eminently qualified geologists have been successful and currently the number proposed for membership has increased greatly. The main problem at the moment is to maintain the international character of the Society.

The Program Policy Committee, established in 1957, to provide continuity in program planning has proved a wise step. One of the first fruits is the symposium on stable isotope research in the field of ore deposits arranged for the Pittsburgh meeting, November 1, 1959.

The need for emphasis on research in economic geology has long been recognized and a Research Committee was appointed during the year with results

noted in the Secretary's report. The future success of the committee in stimulating research in the field of economic geology will be a measure of the extent to which the object of the Society as stated in Article III of the Constitution is fulfilled. All members should consider it a duty to assist in the work of the research committee and of all officers and committees.

The Society is greatly indebted to the Secretary and the Treasurer for their conscientious service given without reward other than the appreciation of the membership.

GEORGE M. SCHWARTZ
President

Report of the Secretary

Two technical meetings were held during the Society Year 1958: the Annual Meeting with the Geological Society of America and associated societies, November 6–8, 1958, in St. Louis, Missouri; the other with the American Institute of Mining, Metallurgical, and Petroleum Engineers, February 15–19, 1959, in San Francisco, California. The program and abstracts of papers presented at the November meeting are printed in the November 1958 issue of ECONOMIC GEOLOGY. The Presidential Address, "Hydrothermal alteration," was delivered by President George M. Schwartz in St. Louis on November 8. The program for the February meeting is given below. Abstracts of papers presented at this meeting are printed in the December 1958, January and February 1959 issues of Mining Engineering.

Technical program—San Francisco meeting, February 1959 presented in conjunction with the AIME

WEDNESDAY, FEBRUARY 18, 9:00 A.M.

Joint Program, Society of Economic Geologists and Industrial Minerals Div., SME

1. Geology of the Montgary Pegmatite—Richard W. Hutchinson, Toronto, Canada.
2. Environmental Factors Governing the Origin and Distribution of Heavy-Mineral Deposits on Padre Island, Texas, A Barrier Island—Louis Moyd, Yonkers, New York.
3. Thorite and Rare Earth Deposits in the Lemhi Pass Area, Lemhi County, Idaho—Alfred L. Anderson, Department of Geology, Cornell University, Ithaca, New York.
4. Radiographic Distribution Analysis Applied to Uraniferous Pyrite, Galena, and Sphalerite—H. D. Wright, J. J. Hutta, W. P. Shulhof, C. M. Smith, The Pennsylvania State University, University Park, Pennsylvania.
5. Economic Uranium Deposits in Granitic Dykes, Bancroft District, Ontario—S. C. Robinson, Geological Survey of Canada, Ottawa, Canada.

WEDNESDAY, FEBRUARY 18, 2:00 P.M.

Society of Economic Geologists

1. Relation of Magnetic Anomalies to Some Geologic Structures in Northern Minnesota—Gordon D. Bath, U. S. Geological Survey, Menlo Park, California.
2. Aeromagnetic Effects of Igneous Features in Northern Minnesota—George M. Schwartz, Minnesota Geological Survey, University of Minnesota, Minneapolis, Minnesota.

3. Structural Environment of the Illinois-Kentucky Fluorspar District—M. P. Nackowski, Salt Lake City, Utah.
4. Structures Related to Solution of Borax at Kramer, California—Ward C. Smith, U. S. Geological Survey, Claremont, California.
5. The Alhambra Cobalt-Nickel-Silver Deposit, Black Hawk (Bullard Peak) District, New Mexico—Elliot Gillerman, Department of Geology, University of Kansas, Lawrence, Kansas.
6. A Concept of the Origin of Porphyry Copper Deposits—C. Wayne Burnham, Department of Geology, The Pennsylvania State University, University Park, Pennsylvania.

THURSDAY, FEBRUARY 19, 9:00 A.M.

Joint Program, Society of Economic Geologists and Geology Unit, Mining and Exploration Division, SME

1. Deposits of the Manganese Oxides—D. F. Hewett, U. S. Geological Survey, Menlo Park, California.
2. Geochemical Study of Lead-Zinc-Silver Ore from the Darwin Mine, Inyo County, California—Wayne E. Hall, U. S. Geological Survey, Menlo Park, California.
3. Genesis of the Scott Magnetite Deposit, Sterling Lake, New York—A. F. Hagner, L. G. Collins, and Tin Aye, Department of Geology, University of Illinois, Urbana, Illinois.
4. Tectonic Analysis as an Exploration Tool—Peter Coles Badgley, Colorado School of Mines, Golden, Colorado.
5. Quantitative Mineralogy as a Guide to Exploration—R. J. P. Lyon, Kennecott Copper Corporation, Salt Lake City, Utah.

The Proceedings of the Society for the years 1954–57, and an up-to-date list of members, was printed and distributed to the membership in October 1958. The document shows that during the interval 1954–57, the number of members increased from 764 to 941, or roughly 23 percent, and that the membership now includes representatives from 46 countries distributed by regions as follows: North America (including Hawaii and the Islands of the Caribbean) 82.6 percent; Europe (including the United Kingdom) 6.2 percent; Africa 3.4 percent; South America 2.9 percent; Australia 2.9 percent; and Asia (including the Philippine Islands) 2 percent.

The Council met at St. Louis on November 7, and again in San Francisco on February 19.

The following committees were approved for the Society Year 1959:

Program Committee
Robert M. Grogan, Chairman
Donald E. White
M. L. Jensen
James P. Pollock
J. S. Stevenson
A. E. J. Engel
Delos E. Flint
H. M. Bannerman, ex-officio

Admissions Committee
Frank C. Foley, Chairman
Patrick M. Hurley
R. B. Fulton
Charles F. Park, Jr.
James E. Thomson

Program Policy Committee
Hugh M. Roberts, Chairman
Charles A. Anderson

Charles F. Park, Jr.
Ralph Marsden
James P. Pollock
Weston Bourret

Research Committee
Charles Meyer, Chairman
Robert Follinsbee
Richard M. Foose
Robert M. Garrels
J. M. Harrison
Herbert E. Hawkes
Mead L. Jensen
S. E. Jerome
Vincent C. McKelvey
Lester G. Zeihen

Publications Committee
Richard M. Foose, Chairman
John H. Ffolliott
Eldred D. Wilson

Auditing Committee
Francis G. Wells, Chairman
A. Nelson Sayre

Finance Committee
Joseph T. Singewald, Jr., Chairman
Olaf N. Rove
Donald M. Fraser

Nominating Committee
William H. Callahan, Chairman
Roger H. McConnel
F. S. Turneaure

Penrose Medal Award Committee
Clayton G. Ball, Chairman
Morris M. Leighton
John W. Vanderwilt
Thomas L. Kesler
Joe Webb Peoples

Representatives to AAAS
W. H. Bradley
Ralph S. Cannon

Representative to National Research Council
Walter S. White

In addition, Donald E. White was appointed to serve as Society representative to the Office of Critical Tables, National Academy of Science, to advise on problems relative to the revision of the Critical Tables.

Necrology

The Society regrets the loss of the following members through death:

Oliver Bowles, elected 1946, died August 1958
Frank Fitch Grout, Charter Member, Senior Member, died July 31, 1958
Robert M. Overbeck, elected 1930, died September 23, 1958
David Bright Reger, elected 1931, died September 10, 1958
Taisia M. Stadnichenko, elected 1947, died November 25, 1958
Thorolf Vogt, elected 1934, died December 8, 1958
Robert Tunstall Walker, elected 1946, died January 1957
Alexander Newton Winchell, Charter Member, Senior Member, died June 7, 1958

New Members

Thirty-two nominees were elected to membership as follows:

Allen F. Agnew
Donald Clark Bulmer
Harry Beard Cannon
Russell Henry Wood Chadwick
Garth M. Crosby
Ferdinand Friedensburg
Harry Clifford Granger
Carlyle Gray
John Jesse Hayes
Everett D. Jackson

David Lamphere Kendall
Keith B. Ketner
Alvin Leonard Lugn
Thomas Crockett Marvin
William Meredith Merrill
Robert W. Metsger
Robert P. Morrison
Albert Ernest Moss
John Barratt Patton
John David Pelletier
Robert Grier Lefevre Reeves
Uuno M. Sahinen
Daniel Reeves Shawe
Richard Porter Sheldon
Douglas Maynard Sheridan
William Spackman
Robert Harnden Stebbins
Frederick Morrill Swain, Jr.
Caesar Voute
Woodville Joseph Walker
Quentin Gellibrand Whishaw
Richard Vaughn Wyman

Resignations

Six members resigned.

Lloyal O. Bacon, elected 1954
C. H. Hopper, elected 1945
Frank A. Morgan, elected 1951
Hendrik Jan Schuiling, elected 1930
W. S. Tangier Smith, elected 1941
Douglas G. H. Wright, elected 1924

Senior Members

Under Article V, Sec. 4 of the Constitution the following members were designated Senior Members:

Kenneth C. Heald, Charter Member 1921
John B. Mertie, Jr., Charter Member 1922
Fred Searls, Jr., elected 1922
Paul Weaver, elected 1922

The Society elected the following members to serve as officers for the periods indicated:

President, 1960 — Duncan R. Derry

Vice President, 1960 — Charles F. Park, Jr.

Regional Vice-Presidents, 1959

North America — J. Ruben Velasco
South America — Victor M. Lopez
Europe — Kingsley Charles Dunham
Asia — Luis Santos-Yñigo
Australia — Haddon F. King
Africa — A. Paul Gerhard Sohnge

Councilors, 1959–61

Vincent D. Perry
Stanley Davidson
Desmond F. Kidd

The report of a Special Committee on the revision of the Constitution and By-Laws, appointed in 1957, was presented to the Council at the November meeting by the Chairman, Francis Cameron. This report has been taken under advisement by the Council, and, as approved by the Council, the various suggestions for modifications of the Constitution will be submitted to the membership for ratification.

Acting upon the advice of an *ad hoc* committee, set up in 1957, and with Council approval, the President appointed a continuing Committee on Research to study ways and means by which the Society can best contribute toward the stimulation of research vital to the advancement of economic geology. In an interim report presented to the Council at the San Francisco meeting, the Research Committee advised that it was giving particular attention to three major problems: 1) the need to seek out and give recognition to "outstanding achievements on the part of individuals doing research"; 2) ways and means by which "to improve communications between research workers and practicing geologists"; and 3) ways and means by which the Society might aid in supporting "specific research programs or projects by bringing together the three essential elements for research—the man, the idea and the facilities."

As an initial step in an attack on the first of these problems, the Committee recommended, and the Council approved, a plan whereby the Society will award annually a citation and a prize of $100 *"to a geologist whose research as a University student results in a paper of high merit on a subject judged important to economic geology."*

At the November meeting the Council approved a recommendation by the Committee on Program Policy, that the Society sponsor a symposium on "The role of stable isotope research in the field of ore deposits," said symposium to be scheduled at a special session of the Society during or just prior to the opening of the November 1959 meetings of the GSA and associated societies. At the San Francisco meeting the Committee on Programs presented, and the Council approved, preliminary plans for this symposium. Council also approved a recommmendation that the symposium be held at Pittsburgh on Sunday afternoon and evening, November 1, i.e. the day before the opening of the GSA meetings, and that arrangements be made to hold a Society dinner at the William Penn Hotel, Pittsburgh, Sunday evening, November 1.

On the advice of the Penrose Award Committee, the Council also approved rules to govern the nomination of candidates for the Penrose Medal for Economic Geology as follows:

A. The Penrose Medal is awarded for "unusual original work in the Earth Sciences." While no formal rules exist concerning eligibility, it is considered that a candidate should be a person of outstanding accomplishment in the profession of economic geology (though not necessarily a member of the Society) who is able and willing to present himself in person to receive the award at the time of nomination. The death of a candidate subsequent to June 15 (of the year of his selection), however, does not render him ineligible and, if selected for the award, the presentation may be made posthumously. In considering their nominations, members may wish to refer to Article III of the Constitution of the Society, which clearly define the object of the Society.

B. Nominations by members of the Society are to be submitted in quintuplicate to the *Chairman of the Penrose Award Committee*, who will promptly acknowl-

edge receipt of each nomination and distribute a copy to each of the other members of the Committee. It is requested that nominations be prepared according to the following outlines:

(1) Name, office or title, and affiliation of nominee.
(2) His date and place of birth, education, degrees, honors, and awards.
(3) Major events in his professional career, including bibliography.
(4) Outstanding achievements and accomplishments which warrant his nomination.

C. Nominations may be submitted *at any time up to a final deadline of June 15,* after which the list of nominations will be closed. The recipient of the Award will be announced at a suitable time thereafter by the Council.

A copy of these rules and an invitation to the membership to nominate candidates for the 1959 Award was sent forthwith to all members of the Society.

HAROLD M. BANNERMAN
Secretary

Report of Treasurer for Fiscal Year Ending November 30, 1958

Receipts and Expenditures

Receipts

Dues	$6,551.08
Life Memberships	300.00
Initiation Fees	290.00
Net Investment Income	5,774.05
Annotated Bibliography (from National Academy of Sciences)	107.49
Total Receipts	$13,022.62
Cash on hand, December 1, 1957	6,690.83
Total	$19,713.45

Expenditures

Secretary Expenses	$ 3,060.52
Treasurer Expenses	480.97
Economic Geology Publishing Company Journal Subscriptions	4,620.34
Economic Geology Publishing Company Society Notices	148.75
Miscellaneous	72.38
American Geological Institute Contribution	550.00
Transferred to Portfolio	1,990.36
Total Expenditures	$10,923.32
Cash on hand, November 30, 1958	8,790.13
Total	$19,713.45

Portfolio November 30, 1958

		Book Value	*Market Nov. 30*
Stocks			
55 shares	Allied Chemical and Dye Corporation ..	$ 5,024.74	$ 4,950.00
660	Aluminum Limited	12,906.71	21,202.50
143	American Telephone and Telegraph	20,097.33	28,600.00
120	Baltimore Gas and Electric	3,310.88	5,205.00
106	Dow Chemical Company	4,165.98	7,817.50
100	Ford Motor Company	6,119.30	4,825.00
100	General Motors	4,437.00	4,900.00
79	Gulf Oil Corporation	4,381.76	9,470.12
152	Pacific Gas and Electric Company	5,289.35	9,196.00
462	Standard Oil Company of California	4,641.29	27,835.00
100	Standard Oil Company of Indiana	3,900.78	4,800.00
2	Standard Oil Company of New Jersey	—	118.75
408	Texas Company	5,366.88	34,935.00
110	United Gas Corporation	3,088.88	3,800.00
10	Christiana Securities, cum. pfd.	1,277.50	1,300.00
	Total	$84,008.38	$168,955.37
Bonds			
5000	Cleve. Cinn. and St. Louis, E 4/12s, 1977	4,729.50	3,475.00
5000	Erie Railroad, A 4 1/2s, 2015	4,925.00	2,693.75
1600	Am. Tel. and Tel., conv. deb 4 1/4s, 1973	1,603.14	2,524.00
	Total	$11,257.64	$ 8,692.75
	Cash in Custodian Account	1.94	1.94
	Total Portfolio	$95,267.96	$177,650.06

12 shares Economic Geology Publishing Company stock with a par value and a market value of $300.00 are not included in the marketable securities of the Society but are deposited with the Custodian.

Endowment Fund

Balance December 1, 1957	$ 29,848.02
Life Memberships	300.00
Balance November 30, 1958	$ 30,148.02

Penrose Medal Fund

Balance December 1, 1957	$ 5,663.56
Income from investments	350.59
Balance November 30, 1958	$ 6,014.15

Annotated Bibliography Fund

Balance December 1, 1957	$ 2,687.78
Received	107.49
Balance November 30, 1958	$ 2,795.27

The receipts are royalties on "Ore Deposits as Related to Structural Features" received from the National Academy of Sciences.

Sustaining Fund

Balance December 1, 1957	$ 50.00
Balance November 30, 1958	50.00

Voluntary contributions subject to order of Secretary.

Surplus Fund

Received from Dues	$ 6,551.08
Received from Initiation Fees	290.00
Income from Members	$ 6,841.08
Operating Expenses	8,932.96
Excess of Expenses over Current Income from members	−2,091.88
Income from Investments (less Penrose Medal Share)	+5,423.46
Total to Surplus	3,331.58
Balance December 1, 1957	61,719.07
Balance November 30, 1958	$ 65,050.65

Assets and Liabilities

Assets

Book Value of Portfolio	$ 95,267.96
Cash in Checking Account	8,790.13
	$104,058.09

Liabilities

Endowment Fund	$ 30,148.02
Penrose Medal Fund	6,014.15
Annotated Bibliography Fund	2,795.27
Sustaining Fund	50.00
Surplus Fund	65,050.65
Total	$104,058.09

The market value of the securities is $82,382.10 in excess of the book value, so that the market value of the assets is $186,440.19.

The net income on investments was 6.06% on the book value and 3.25% on the market value of the securities as of November 30, 1958.

JOSEPH T. SINGEWALD, JR.
Treasurer

Economic Geology
Vol. 54, 1959, pp. 1148–1150

SCIENTIFIC NOTES AND NEWS

A group of organic and petroleum geochemists plan to organize an ORGANIC GEOCHEMISTRY SECTION within THE GEOCHEMICAL SOCIETY to offer a common forum for research workers active in the various fields of organic and petroleum geochemistry. Recent advances in these fields indicate the desirability of the exchange of ideas and of their coordination with modern concepts of inorganic geochemistry and geology. The interest shown by earth scientists in The General Petroleum Geochemistry Symposium, recently held at Fordham University, supports this view.

Plans are being made to organize the Organic Geochemistry Section at the 1959 annual meetings of the Geological Society of America and The Geochemical Society in Pittsburgh, Penn., November 2–4. Information may be obtained from the members of the Interim Executive Committee listed below. The members of this committee invite suggestions and comments regarding this matter. It would be helpful if interested individuals could, in advance of the annual meeting, signify their intention to affiliate with the Section, whether or not they plan to attend the meeting.

The only requirements for affiliation with the Section are membership in the Geochemical Society and an interest in organic geochemistry. Membership in the society is open to individuals who have a bachelor's degree or its equivalent in a natural science and an interest in applying that science to geologic problems. Dues are $2.00 per year. Application blanks can be obtained from the Secretary, Prof. Konrad B. Krauskopf, Department of Geology, Stanford University, Calif.

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Berkeley 4, Calif.

PARKE A. HODGES, Vice President, DOUGLAS D. DONALD, and ALLAN M. SHORT of Behre Dolbear & Company are conducting a mineral reconnaissance in Haiti.

LYNWOOD H. WARWICK has retired after 51 years of service in the division of Mineral Resources, Dept. of Conservation and Economic Development, Charlottesville, Va.

A grant of approximately $10,000 from the National Aeronautics and Space Administration has been awarded to Boston University's astronomy and physics department for the study of tektites, the black, glassy fragments of unknown origin, found on the earth's surface. Under the direction of Dr. Gerald S. Hawkins of Cambridge, Mass., the research project will attempt to determine whether the fragments are earth-formed or extra-terrestrial in origin.

A. LINCOLN WASHBURN has moved from Hanover, N. H., to the Department of Geology, University of Canterbury, Christchurch, New Zealand. His home address is 110 Main Road, Redcliffs, Christchurch, New Zealand.

GEORGE D. BELLOWS has been elected a vice president of the Paul Weir Company, Inc., consulting mining engineers with principal offices in Chicago. During the past two years, Mr. Bellows has been in charge of the Ferrous and Non-Ferrous Mining Department of the Paul Weir Company's organization in Korea where the firm is a member of a consortium of engineering companies supplying technical assistance to the government of the Republic of Korea and to the United States Operations Mission to Korea.

RICHARD V. WYMAN has resigned his position as vice president of Western Gold and Uranium, Inc. and is now president of Intermountain Exploration Company, engaged in mining exploration in the southwest.

GEORGE A. KIERSCH, engineering geologist, Oakland, California, spent much of May and June in Norway on geological work connected with a series of proposed construction sites. While there, Dr. Kiersch presented a series of 8 lectures on engineering geology to the students and faculty of the Technical University of Norway, Trondheim. The Norwegian civil engineering student is required to take more training in geology than in most schools in this country and students, faculty, and the practicing engineers have a keen interest in geology and its application in engineering practice.

The NATIONAL SCIENCE FOUNDATION announces that it will continue to support the following programs during the summer of 1960 and the academic year 1960–61: "Undergraduate Research Participation," "Research Participation for Teacher Training," "Science Training for Secondary School Students." Colleges, universities, and other educational institutions desiring to consider participation in these programs may receive full information by addressing: Special Projects in Science Education, Scientific Personnel and Education, Washington 25, D. C.

DONALD W. LINDGREN of St. Paul, Minnesota, formerly chief mining geologist, Northern Pacific Railway, and ERNEST K. LEHMANN of Minneapolis, Minnesota, formerly consulting mining geologist, announce the formation of the partnership Lindgren & Lehmann, Consulting Mining Geologists.

AARO E. AHO is presently in Surinam, Dutch Guiana, consulting on a mining exploration project for a firm in British Columbia.

R. H. HALLAM, JR., has resigned as mine geologist for United Keno Hill Mines, Ltd., Yellowknife Territory, and has accepted a similar position with Campbell Chibougamau Mines, Ltd., Chibougamau, Quebec.

R. E. WHITMORE, former chief geologist with Heath Steele Mines, Ltd. at Newcastle, N.B., Canada, is now at 905 Kingsmere, Ottawa 3, Ontario.

J. MCLAREN FORBES is on a consulting job for Cerro de Pasco Corp. and will be working for them out of New York for the next few months.

R. J. CLAUS is now managing director, Cia Desenvolvimento de Industrias Minerais, Rio de Janeiro, Brazil. He was formerly geologist for Union Carbide Ore Co.

CHARLES K. BROWN, geologist for Aluminum Co. of America, transferred from Bauxite, Arkansas, to the main office in Pittsburgh, Penn.

M. F. GOUDGE of Ottawa, Canada, has been elected a director of American Nepheline Ltd., Toronto. He recently retired as chief of the Industrial Minerals

Division of the Canadian Dept. of Mines at Ottawa having served in this capacity since 1923.

CHARLES A. ANDERSON has been appointed Chief Geologist of the U. S. Geological Survey, a position recently vacated by Dr. Wilmot H. Bradley, appointed in 1944. Dr. Anderson began his career with the U.S.G.S. in 1942 serving as assistant chief and later as chief of the Mineral Deposits Branch.

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For description of Professor Sampson's method, see Economic Geology, Vol. 51, No. 5, August, 1956. *Write for Bulletin SP-131*

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CONTENTS

Part I

FOREWORD ii
ECONOMIC GEOLOGY ..... *Alan M. Bateman* 1
METALLOGENETIC PROVINCES AND EPOCHS ..... *F. S. Turneaure* 38
THERMAL SPRINGS AND EPITHERMAL ORE DEPOSITS ..... *Donald E. White* 99
THE CLASSIFICATION OF ORE DEPOSITS ..... *James A. Noble* 155
STRUCTURE OF HYDROTHERMAL ORE DEPOSITS ..... *H. E. McKinstry* 170
THE ZONAL THEORY OF ORE DEPOSITS ..... *Charles F. Park, Jr.* 226
TEMPERATURES IN AND NEAR INTRUSIONS ..... *T. S. Lovering* 249
SYNTHETIC MINERALS ..... *W. A. Weyl* 282
HYDROTHERMAL ALTERATION AS A GUIDE TO ORE ..... *George M. Schwartz* 300
OXIDATION OF COPPER SULFIDES AND SECONDARY SULFIDE ENRICHMENT ..... *Charles A. Anderson* 324
METHODS AND PROBLEMS OF GEOLOGIC THERMOMETRY ..... *Earl Ingerson* 341
SEDIMENTARY DEPOSITS OF RARE METALS ..... *Konrad B. Krauskopf* 411
ORIGIN OF URANIUM DEPOSITS ..... *V. E. McKelvey, D. L. Everhart and R. M. Garrels* 464

Part II

ENGINEERING GEOLOGY—A FIFTY YEAR REVIEW ..... *Robert F. Legget* 534
INFLUENCE OF GEOLOGICAL FACTORS ON THE ENGINEERING PROPERTIES OF SEDIMENTS ..... *Karl Terzaghi* 557
RECENT DEVELOPMENTS IN CLAY MINERALOGY AND TECHNOLOGY ..... *Ralph E. Grim* 619
PROPERTIES OF CALCIUM AND MAGNESIUM CARBONATES AND THEIR BEARING ON SOME USES OF CARBONATE ROCKS ..... *D. L. Graf and J. E. Lamar* 639
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